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# Canadian Journal of Research

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VOLUME 2

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## THE RELATIONSHIP BETWEEN MORPHOLOGIC CHARACTERS AND RUST RESISTANCE IN A CROSS BETWEEN EMMER, (*TRITICUM DICOCCUM*) AND COMMON WHEAT, (*TRITICUM VULGARE*)<sup>1</sup>

BY J. B. HARRINGTON<sup>2</sup>

### Abstract

A study of morphologic character in relation to field resistance to black stem rust of wheat (*Puccinia graminis tritici*, Erikss. & Henn) was made on the cross Vernal (*Triticum dicoccum*, Schubl.) × Marquis (*T. vulgare*, Host.). Fifteen morphologic characters were used including spike form, spike compactness, stem hollowiness, rachis articulation, rachis width, spikelet adherence, glume adherence, keel sharpness and seed character, all of which are of species differentiating importance. A random group of 276 F<sub>2</sub> plants showed no strong or moderately strong correlations between rust reaction and other characters: the most significant correlation coefficients ranged from .13 to .27. Between any two morphologic characters no strong relationships were found, the highest correlation coefficient obtained being .37. In the entire F<sub>2</sub> population of 21,480 plants there were 232 *vulgare*-like hybrids showing the high rust resistance of Vernal, although Marquis had a fairly uniform infection of moderate severity. All of these hybrids proved, upon laboratory examination, to be of *vulgare* or near-*vulgare* type in nearly all characters especially the economically important characters spike form, rachis articulation, spikelet adherence and glume adherence. This study, therefore, demonstrates that high rust resistance can be transferred from *dicoccum* to a *vulgare*-type wheat without great difficulty. It is concluded that the attainment of desirable combinations of emmer rust resistance with important morphologic characters of *vulgare* depends primarily upon having a population of many thousands of individuals from which to select.

### Introduction

The attainment of desirable *vulgare* wheats having very high resistance to black stem rust (*Puccinia graminis tritici*, Erikss. and Henn.) requires the transference of resistance from a wheat with 14 pairs of chromosomes to one with 21 pairs by means of hybridization. From the breeding standpoint there are two

<sup>1</sup> Manuscript received March 10, 1930.

Contribution from the laboratories of the University of Saskatchewan, Canada, with financial assistance from the National Research Council of Canada. This study forms a part of a co-operative attack on the problem of cereal rust in Canada, carried on jointly by the National Research Council, the Federal Department of Agriculture and the Universities of Manitoba, Saskatchewan and Alberta. The results were reported in full at the Meeting of the Associate Committee on Cereal Rust at Winnipeg on April 9, 1929.

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good illustrations of economically desirable rust resistant varieties obtained from crosses between 28 and 42-chromosome wheats. One of them is the *vulgare* variety Marquillo produced by Hayes and his co-workers in Minnesota from a *durum*  $\times$  *vulgare* cross. The other is the *vulgare* variety Hope produced by McFadden of South Dakota from a *dicoccum*  $\times$  *vulgare* cross. Both of these varieties are now used commercially in their respective places of origin.

Owing to the demand in Western Canada for more satisfactory rust resistant wheats than Marquillo, Hope and their sister strains, several crosses were made by the writer in 1925. One of these was between Marquis (*T.vulgare*) and Vernal (*T.dicoccum*), the latter being almost immune from black stem rust in the field. It was shown by the writer and W. K. Smith (1) in 1928 that this cross furnished exceptionally favorable material for the study of rust reaction in relation to important morphological characters, and for the economic attainment of a desirable rust resistant wheat.

The Vernal  $\times$  Marquis cross was made in sufficiently extensive manner to furnish a very large  $F_2$  population since the need of a large population was evident from the results of previous work. Sax (8) studied a very small population from a *durum*  $\times$  *vulgare* cross and found no *vulgare* segregates possessing rust resistance. Hayes, Stakman and Aamodt (2) grew many thousands of  $F_2$  plants from a *durum*  $\times$  *vulgare* cross and obtained numerous *vulgare* segregates that approached the durum parent in rust resistance. Thompson and Hollingshead (12) in a study of 210  $F_2$  hybrids from a *dicoccum*  $\times$  *vulgare* cross, found only one plant with all of six important morphological characters in the *vulgare* or intermediate-*vulgare* condition. McFadden (5) grew a very large population from a *dicoccum*  $\times$  *vulgare* cross and obtained many *vulgare* plants possessing the *dicoccum* resistance to rust.

### Materials and Methods

In 1928 an  $F_2$  population of 21,480 plants of Vernal (Sask. 1289)\*  $\times$  Marquis (Sask. 1221)\* was grown to maturity in the nursery from a total of 35,800 seeds sown. Late sowing allowed an even stem rust epidemic of moderate strength to develop, making possible an accurate classification of plants on the basis of field rust reaction. As in 1927, physiologic forms 21 and 36 appeared to be the most prominent. All of the plants growing in the first 20 rows of one series of the Vernal  $\times$  Marquis  $F_2$  were taken for genetical study. These plants, 276 in all, constituted a random sample of the entire population; they will be referred to as the "random group". In addition to this material, plants having combinations of characters of infrequent occurrence in the random group were harvested from the entire population for genetical study. Notable in this connection was the finding of 232 plants which were immune from rust in the field and *vulgare*-like in most characters, particularly those of economic importance that are easily observable in the field.

\* These strains of Vernal and Marquis are pure line selections, the former made at Saskatoon, Saskatchewan and the latter at Rosthern, Saskatchewan.



Each plant of the random sample and of the immune *vulgare*-like group was studied with respect to field rust reaction and 15 morphological characters. These morphological characters were chosen on the basis of their use in previous studies of inter-species hybrids and because of the distinct differences of their expression in the varieties Marquis and Vernal. The relationships between field rust reaction and the various morphological characters as well as between some of the latter were examined. The 16 characters and the basis for the classification of the hybrid plants are described in Table I. For each of the characters the hybrids were classified into five groups, viz: D, or those resembling the Vernal (*dicoccum*) parent; ID, or those approaching the Vernal parent; I, or plants intermediate between Vernal and Marquis for the character in question; IV, or plants approaching Marquis; and V, or those resembling the Marquis (*vulgare*) parent.

TABLE I

DESCRIPTION OF THE CHARACTERS STUDIED AND THE CONDITION OF PLANTS OF THE PARENT VARIETIES AND OF  $F_1$  WITH RESPECT TO THESE CHARACTERS

Character	Marquis	Vernal	$F_1$
Field rust reaction.	Susceptible.	Highly resistant.	Resistant.
Spike form (width ratio of lateral side to dorsi-ventral side).	.75 - .83	1.5 - 1.7	1.2 - 1.3
Spike compactness (average length of 10 central internodes).	5.1 - 5.4 mm.	3.4 - 3.8 mm.	4.9 - 5.1 mm.
Stem hollowness (taken 2 cm. below the collar).	Hollow with thin walls.	Solid.	Hollow.
Rachis articulation.	Difficult.	Easy.	Difficult.
Adherence of spikelet to rachis.	Easily detached.	Detached with much difficulty.	Like Vernal.
Lower width of rachis segment.	1.9 - 2.1 mm.	.9 - 1.0 mm.	1.9 - 2.1 mm.
Stem thickness (taken 2 cm. below the collar).	1.9 - 2.1 mm.	.9 - 1.0 mm.	1.7 - 1.9 mm.
Glume adherence.	Easily detached.	Detached with difficulty.	Intermediate.
Rachis hairiness (marginal).	Hairs present full length.	No hairs.	Hairs on upper half only.
Shoulder width of glume.	Wide.	Narrow.	Intermediate.
Shoulder shape.	Slightly sloping.	Quite elevated.	Like Vernal.
Glume shape (length vs. width).	Length almost twice the width.	Length is three times width.	Length slightly more than twice width.
Keel sharpness (angle shown by cross section of lower half).	Obtuse.	Acute.	Acute.
Awning.	Tip awned.	Awned.	Tip awns, longer than Marquis.
Seed character.	Short, plump with round cheeks and wide deep crease.	Long, narrow with angular cheeks and narrow, shallow crease.	Resembles Vernal more than Marquis.

NOTE:—For each of the 16 characters the hybrids were classified into five groups, viz: D or those resembling Vernal. I or those intermediate between Vernal and Marquis, V or those resembling Marquis, ID or those intermediate between D and I, IV or those intermediate between I and V.

## Results

### *Analysis of the Random Group of F<sub>2</sub> Plants*

Space does not permit the reproduction here of all of the results obtained from the random lot of F<sub>2</sub> plants. The results from the first 85 plants studied are given in Table II. The combinations of characters vary with every plant and in practically every way. Culture 2046 is a good illustration of a predominantly *vulgare*-like plant that was immune from rust in the field and culture 2047 is a *dicoccum*-like plant that was also immune. Culture 2053 is a *vulgare*-like plant having as much rust susceptibility as Marquis. Cultures 2048 and 2049 are *dicoccum*-like in nearly all characters whereas cultures 2052 and 2056 are *vulgare*-like in all but a few characters. Other cultures, such as 2054 and 2055, exhibit about as many *vulgare* as *dicoccum* characters.

A casual inspection of Table II gives the impression that *dicoccum* characters appear much more frequently than *vulgare* characters, and, according to previous work, this was to be expected. A determination of the relative proportions of *vulgare*-like and *dicoccum*-like plants showed an average proportion of 5.4 to 1.0, respectively, as given in Table III. With less than a sixth of the plants *vulgare*-like and a part of these susceptible to rust, the proportion of highly resistant strongly *vulgare*-like plants was very small.

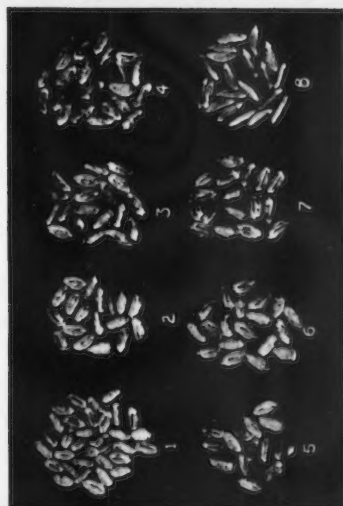
### *Study of Highly Resistant F<sub>2</sub> Plants of Vulgare Type*

The entire population of 21,480 F<sub>2</sub> plants grown to maturity in the field contained 232 plants that appeared to be of *vulgare* type and showed no rust infection although Marquis checks had a moderately heavy infection. The immune *vulgare*-like plants proved upon laboratory examination to be V, IV or I in nearly all characters; especially the economically important characters spike form, rachis articulation, spikelet adherence and glume adherence. Table IV gives a detailed description of 24 of these plants. The first eight were very vigorous in the field and set large amounts of seed allowing them to be tested to several rust forms in the greenhouse. The remaining plants in the table are fairly representative of the whole *vulgare*-like group. Plate I-1 shows spikes of representative *vulgare*-like resistant plants. Representative stems of Vernal, Marquis and the resistant hybrids of *vulgare*-type appear in Plate I-2. The seed of the hybrids shown in Plate I-1 is compared with seed of the parent varieties in Plate I-3. These three figures illustrate the attainment of high rust resistance in combination with *vulgare* spike and seed characters.

Returning to Table IV it is apparent that the distribution of the occasional *dicoccum* or near-*dicoccum* characters is more or less fortuitous. Plant 2322 has the typical articulate rachis of *dicoccum*. Plant 2323 has a tenacious rachis, wholly *vulgare*-like but approaches *dicoccum* in spikelet adherence and is awned like Vernal. Plant 2335 has a narrow shoulder and long awns like Vernal and the typical *dicoccum* seed shape. In all others of the 15 characters studied,



B. Spikes of representative Vernal  $\times$  Marquis  $F_2$  hybrids that equalled Vernal in stem rust resistance in the field, and were morphologically of vulgare type. 5, 6 and 7 are hybrids taken at random from the group of vulgare-like plants that showed Vernal resistance. 8 is Vernal.



C. Seed of the plants the spikes of which are shown in A and B. 1 is Marquis; 2, 3, 4, 5, 6 and 7 are hybrids numbered as in A and B; 8 is Vernal (as the seed of Vernal does not thresh free from the investing chaff it was removed by hand).



A. Spikes of representative Vernal  $\times$  Marquis  $F_2$  hybrids that equalled Vernal in stem rust resistance in the field, and were morphologically of vulgare type. 1 is Marquis; 2, 3 and 4 are hybrids taken at random from the group of vulgare-like plants that showed Vernal resistance.

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THE  
HISTORY  
OF  
THE  
CITY  
OF  
NEW  
YORK



FROM  
THE  
ORIGINAL  
MANUSCRIPT  
OF  
JONAS  
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THE  
HISTORY  
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YORK



TABLE II

DESCRIPTION OF A PORTION OF THE PLANTS FROM A RANDOM LOT OF  
276 VERNAL  $\times$  MARQUIS  $F_2$  PLANTS GROWN IN THE FIELD

Line No.	Field rust reaction	Spike form	Spike compactness	Stem hollowness	Rachis articulation	Spikelet adherence	Rachis width	Stem thickness	Glume adherence	Rachis hairiness	Shoulder width	Shoulder shape	Glume length-width ratio	Keel sharpness	Awning	Seed character
2046	D	D	V	V	I	I	IV	V	I	I	V	ID	IV	IV	IV	I
2047	D	ID	ID	D	I	D	I	I	I	D	D	ID	D	D	D	D
2048	ID	D	ID	D	D	D	V	I	D	D	D	ID	ID	ID	D	D
2049	D	D	D	D	V	ID	ID	ID	IV	D	I	D	V	V	V	ID
2050	D	D	D	ID	I	I	I	V	ID	D	I	I	V	V	V	ID
2051	I	ID	D	I	I	IV	V	V	IV	D	ID	IV	V	V	IV	I
2052	D	IV	IV	V	ID	IV	V	V	IV	IV	D	IV	V	V	IV	I
2053	V	IV	V	V	V	IV	V	V	IV	V	V	V	V	V	IV	IV
2054	ID	IV	D	ID	V	I	V	IV	V	D	D	IV	V	V	IV	I
2055	D	ID	V	ID	IV	D	V	IV	D	I	I	I	IV	ID	V	V
2056	IV	IV	V	V	IV	V	V	V	V	IV	V	I	I	V	V	D
2057	D	D	D	V	I	V	V	V	D	D	D	V	ID	V	V	D
2058	D	D	D	I	IV	IV	I	ID	IV	D	D	V	D	V	IV	D
2059	ID	IV	D	ID	D	D	ID	ID	D	V	V	ID	ID	IV	V	I
2060	ID	ID	D	D	I	D	I	ID	ID	ID	V	ID	V	V	V	I
2061	D	D	D	D	I	ID	D	ID	I	D	IV	IV	ID	IV	V	D
2062	D	I	D	IV	IV	V	V	V	V	D	ID	ID	D	V	IV	IV
2063	D	I	IV	ID	D	D	ID	I	ID	IV	ID	D	ID	IV	D	ID
2064	D	I	I	ID	D	D	IV	IV	D	I	IV	ID	I	D	I	I
2065	ID	IV	V	IV	I	V	V	V	V	I	V	I	V	D	V	IV
2066	D	D	ID	D	ID	ID	ID	I	IV	D	V	D	I	IV	V	D
2067	D	I	D	ID	I	ID	I	ID	IV	D	D	I	D	V	D	D
2068	D	I	V	V	I	ID	V	V	I	D	V	D	V	I	V	D
2069	D	D	IV	D	IV	D	I	ID	D	ID	D	D	D	ID	ID	ID
2070	D	V	IV	I	IV	IV	I	IV	I	D	D	IV	IV	V	I	I
2071	ID	I	V	IV	IV	ID	IV	V	I	ID	ID	D	D	I	ID	ID
2072	IV	I	V	I	D	D	V	V	D	IV	V	ID	V	D	V	I
2073	D	I	D	I	I	V	ID	I	IV	D	I	V	V	V	IV	I
2074	ID	ID	D	I	I	V	IV	V	V	ID	D	V	V	IV	IV	V
2075	D	D	D	D	ID	IV	ID	I	IV	D	D	I	ID	V	IV	ID
2076	I	D	I	D	I	D	D	D	I	ID	D	ID	D	ID	IV	I
2077	I	I	I	IV	I	V	I	IV	IV	I	D	D	D	V	I	I
2078	ID	ID	IV	I	I	ID	IV	IV	I	ID	I	D	ID	I	ID	ID
2079	D	IV	D	D	I	ID	D	D	I	ID	D	I	D	I	I	I
2080	D	D	D	D	D	ID	I	D	IV	I	D	I	D	D	V	I
2081	D	D	ID	ID	D	ID	ID	I	D	I	IV	IV	ID	ID	IV	D
2082	D	D	D	D	I	D	ID	ID	ID	I	D	ID	IV	D	V	D
2083	I	ID	ID	D	V	V	V	V	ID	D	IV	V	V	V	V	V
2084	ID	I	V	IV	V	IV	V	V	IV	D	V	ID	V	IV	I	ID
2085	D	ID	V	ID	I	D	I	I	D	IV	I	D	ID	D	V	D
2086	ID	D	D	D	ID	D	ID	ID	D	D	V	I	ID	D	ID	ID
2087	D	D	D	D	ID	D	D	D	ID	D	D	D	D	D	D	D
2088	D	ID	V	I	I	D	I	V	D	V	IV	D	ID	I	V	D
2089	D	ID	D	D	I	D	IV	V	ID	I	D	ID	D	V	IV	ID
2090	D	ID	I	I	ID	V	I	IV	IV	D	D	I	D	V	V	ID

\*Sterile

TABLE II—Continued

Line No.	Field rust reaction	Spike form	Spike compactness	Stem hollowness	Rachis articulation	Spikelet adherence	Rachis width	Stem thickness	Glume adherence	Rachis hairiness	Shoulder width	Shoulder shape	Glume length—width ratio	Keel sharpness	Awning	Seed character
2091	D	ID	ID	D	I	V	I	I	V	D	D	V	D	V	D	*
2092	D	ID	V	IV	IV	D	I	IV	ID	V	ID	ID	D	ID	IV	D
2093	D	D	ID	D	D	D	ID	I	ID	D	I	V	D	V	D	D
2094	D	IV	I	I	I	D	I	I	ID	I	ID	V	D	V	D	D
2095	D	I	V	IV	ID	D	I	IV	D	I	IV	I	IV	I	D	D
2096	D	I	D	IV	I	V	IV	V	V	D	D	V	V	V	V	*
2097	D	ID	IV	I	IV	ID	IV	IV	I	D	ID	V	D	D	IV	D
2098	D	D	D	ID	I	D	ID	ID	ID	D	IV	ID	ID	D	ID	D
2099	D	D	IV	I	I	D	ID	D	D	IV	D	V	D	D	D	*
2100	D	ID	D	I	ID	D	I	I	ID	I	V	I	V	ID	IV	*
2101	V	V	I	I	IV	IV	I	V	IV	D	I	I	IV	IV	V	ID
2102	D	I	V	IV	D	D	V	V	D	V	V	ID	IV	D	I	D
2103	D	I	D	V	ID	IV	ID	I	V	D	D	I	ID	I	V	D
2104	D	ID	D	ID	ID	D	ID	I	D	D	IV	I	D	D	V	D
2105	ID	IV	D	V	I	V	V	V	IV	D	V	IV	IV	ID	V	V
2106	D	I	V	IV	I	I	I	IV	IV	IV	ID	I	ID	ID	IV	D
2107	D	D	D	ID	ID	ID	ID	ID	ID	IV	IV	ID	ID	ID	IV	ID
2108	D	I	D	ID	ID	I	ID	ID	IV	D	ID	IV	ID	V	D	ID
2109	D	D	ID	I	ID	IV	I	IV	I	ID	I	V	ID	D	IV	ID
2110	ID	I	ID	I	IV	I	D	I	IV	ID	D	V	D	V	IV	ID
2111	D	ID	ID	D	I	V	IV	V	IV	D	IV	I	I	I	V	ID
2112	ID	ID	D	IV	D	I	I	IV	IV	D	D	ID	ID	D	I	D
2113	D	I	V	V	V	I	I	IV	V	I	ID	V	ID	V	IV	ID
2114	D	D	D	D	I	D	IV	IV	D	D	IV	V	ID	I	D	D
2115	D	D	D	I	D	D	ID	I	D	D	IV	I	IV	V	D	ID
2116	D	ID	D	IV	ID	V	ID	V	V	ID	D	V	ID	V	V	*
2117	D	D	D	D	ID	D	D	ID	D	ID	D	I	D	D	V	ID
2118	D	IV	IV	D	I	D	D	ID	D	D	ID	I	D	I	V	D
2119	D	ID	V	I	I	D	ID	IV	V	ID	ID	I	ID	ID	IV	I
2120	D	ID	ID	I	ID	I	I	I	I	I	I	I	I	I	V	D
2121	D	I	ID	I	ID	ID	I	IV	ID	D	V	V	V	D	IV	D
2122	IV	I	ID	V	I	V	V	V	V	ID	I	V	IV	V	I	IV
2123	D	IV	D	D	IV	IV	ID	IV	D	D	ID	I	IV	V	D	*
2124	D	IV	I	IV	ID	D	IV	V	D	D	ID	ID	IV	I	D	ID
2125	D	D	D	D	D	D	I	IV	D	ID	ID	IV	D	D	D	D
2126	D	I	V	IV	IV	D	V	IV	ID	V	I	I	I	ID	I	ID
2127	D	ID	IV	I	IV	D	I	IV	D	V	IV	ID	IV	IV	V	ID
2128	D	IV	V	IV	IV	IV	I	V	IV	ID	IV	V	V	ID	I	ID
2129	D	I	IV	IV	I	V	IV	V	I	I	V	I	I	ID	IV	ID
2130	D	ID	D	ID	ID	D	ID	I	I	D	D	IV	D	D	D	D

\*Sterile

these three plants were classified as V, IV or I. Plant 2413 differs from those just mentioned in showing no distinctly *dicoccum* resemblances excepting in the relatively unimportant characters, shoulder width and shoulder shape. Similarly *dicoccum* character is approached by Plant 2339 only in shoulder width and by plant 2350 only in spike compactness. Without further reference

to individual *vulgare*-like segregates it seems evident that the securing of a suitable combination of characters depends upon having a sufficiently large number of individuals from which to choose.

#### *Morphologic Characters and Their Inter-relationships*

The following morphologic characters were studied: spike form, spike compactness, stem hollowiness, rachis width, rachis marginal hairiness, rachis articulation, glume adherence, glume shape, shoulder width, shoulder shape, keel sharpness, spikelet adherence, awning, seed character and stem thickness. The classification of the plants of the  $F_2$  random group for each character is shown in Table V. In general the  $F_2$  plants resembled Vernal more than they

TABLE III  
THE DETERMINATION OF THE PROPORTION OF *vulgare*-LIKE HYBRIDS  
IN VERNAL  $\times$  MARQUIS  $F_2$

Basis of classification of $F_2$ plants	No. of $F_2$ plants	Ratio of D, ID and I to I, IV and V
Plants classified as D, ID or I for all of the 16 characters.	10	3.33
Plants classified as I, IV or V for all of the 16 characters.	3	1.00
Plants classified as D, ID or I for all but two of the 16 characters.	54	5.40
Plants classified as I, IV or V for all but two of the 16 characters.	10	1.00
Plants classified as D, ID or I for at least 9 of the 16 characters.	233	5.42
Plants classified as I, IV or V for at least 9 of the 16 characters.	43	1.00
Average proportion for last two sets of determinations.*		5.4 1.0

\*The numbers in the first set of determinations are too small to be accurate.

resembled Marquis (refer to Table III). Considering the characters separately the distribution of the hybrids with regard to resemblance to the parent varieties varied considerably. The large majority of  $F_2$  plants were *dicoccum*-like in field rust reaction. Very few were *vulgare*-like in spike form, seed character or rachis tenacity. Few plants on the other hand, were *dicoccum*-like in stem thickness. For most characters more plants approached the *dicoccum*-type than the *vulgare*-type.

A great many relationships could be worked out where 16 different characters are concerned, but only the most important ones need be considered. Field rust reaction is of maximum interest; consequently its association with each of the other characters was determined as illustrated in Table VI. The correlation coefficient was used throughout the study, for, although the data were not taken on a numerical basis, the five categories used had numerical significance since each differed from the adjacent one by the same amount.



TABLE IV

DESCRIPTIONS OF A PART OF THE 232 APPARENTLY *vulgare*-LIKE PLANTS THAT WERE SELECTED FROM 2266 VERNAL  $\times$  MARQUIS  $F_2$  PLANTS WHICH WERE HIGHLY RUST RESISTANT IN THE FIELD

Line No.	Spike form	Spike compactness	Stem hollowness	Rachis articulation	Spikelet adherence	Rachis width	Stem thickness	Glume adherence	Rachis hairiness	Shoulder width	Shoulder shape	Glume length-width ratio	Keel sharpness	Awning	Seed character
2322	IV	V	IV	D	I	V	V	I	V	V	V	IV	IV	V	I
2323	IV	IV	V	I	ID	V	V	IV	V	V	IV	IV	V	D	IV
2331	I	ID	I	ID	IV	I	V	V	V	IV	I	ID	V	V	D
2335	IV	V	V	I	IV	V	V	V	IV	D	V	IV	V	D	D
2346	IV	ID	IV	IV	V	IV	V	V	I	IV	IV	I	V	V	I
2387	V	V	I	I	I	V	V	IV	I	IV	IV	I	IV	IV	I
2413	V	V	I	I	V	V	V	V	V	ID	ID	I	V	V	IV
2408	IV	I	D	I	V	ID	I	V	ID	V	V	D	I	D	I
2325	IV	V	IV	I	I	I	IV	I	V	I	V	I	V	V	D
2326	IV	V	IV	IV	IV	V	V	I	ID	I	V	I	V	I	ID
2327	IV	V	IV	V	V	I	V	V	V	D	I	I	V	IV	I
2328	IV	V	IV	ID	IV	V	V	IV	V	I	I	IV	V	V	ID
2329	IV	V	I	IV	V	I	V	V	ID	I	I	ID	V	IV	I
2330	IV	ID	I	I	V	IV	I	V	V	D	I	IV	IV	I	ID
2334	I	ID	IV	IV	IV	I	IV	V	IV	D	I	IV	IV	IV	I
2336	I	ID	I	IV	IV	V	V	IV	IV	IV	I	IV	IV	IV	I
2337	IV	IV	IV	IV	IV	IV	V	IV	ID	IV	ID	I	V	V	I
2338	IV	IV	V	D	IV	V	V	I	IV	I	I	V	V	IV	I
2339	V	V	V	V	IV	IV	V	V	V	D	I	IV	V	IV	V
2340	IV	ID	IV	I	V	IV	V	V	V	D	I	ID	V	I	ID
2341	IV	I	V	V	V	V	V	V	I	D	V	D	V	V	I
2344	IV	V	I	IV	D	ID	IV	IV	I	D	IV	V	V	IV	I
2345	IV	I	IV	I	IV	I	V	V	V	IV	I	IV	V	V	ID
2350	IV	D	IV	IV	IV	IV	V	V	IV	IV	I	IV	V	I	IV

TABLE V

THE DISTRIBUTION OF 276 VERNAL  $\times$  MARQUIS  $F_2$  PLANTS WITH RESPECT TO SIXTEEN CHARACTERS

Character	D	ID	I	IV	V
Field rust reaction	212	37	12	10	5
Spike form	91	65	75	37	8
Spike compactness	108	44	31	30	63
Stem hollowness	70	71	70	43	22
Rachis articulation	61	67	90	43	15
Spikelet adherence	132	24	41	34	45
Rachis width	53	63	81	42	37
Stem thickness	17	33	77	79	70
Glume adherence	64	55	52	63	42
Rachis hairiness	117	56	35	37	31
Shoulder width	88	45	53	47	43
Shoulder shape	36	53	100	18	69
Glume shape	92	62	51	44	27
Keel sharpness	67	67	44	34	64
Awning	63	26	41	56	90
Seed character	83	67	44	21	6

TABLE VI

RELATIONSHIP BETWEEN FIELD RUST REACTION AND EACH MORPHOLOGICAL CHARACTER STUDIED IN THE VERNAL  $\times$  MARQUIS  $F_2$

Characters associated with field rust reaction	Coefficient of correlation*
Spike form	.19 $\pm$ .039
Spike compactness	.16 $\pm$ .030
Stem hollowness	.21 $\pm$ .039
Rachis articulation	.19 $\pm$ .039
Spikelet adherence	.15 $\pm$ .040
Rachis width	.24 $\pm$ .038
Stem thickness	.13 $\pm$ .040
Glume adherence	.05 $\pm$ .040
Rachis hairiness	.24 $\pm$ .038
Shoulder width	.13 $\pm$ .040
Shoulder shape	.05 $\pm$ .041
Glume shape	.14 $\pm$ .040
Keel sharpness	.03 $\pm$ .041
Awning	.09 $\pm$ .040
Seed character	.27 $\pm$ .040

\*For number of figures used see Kelley (3) on "How many figures are significant?"

Field rust reaction was found to be associated to a small extent with some morphological characters but strongly related with none of them. The correlation coefficients that exceed three times their probable errors run from .13 to .27, and seven of them are larger than four times their probable errors. As these coefficients are the most significant ones and represent the strongest of the relationships it is of particular interest to examine their correlation surfaces. The morphological characters concerned are spike form, spike compactness, stem cavity, rachis articulation, rachis width, rachis hairiness and seed character. The correlation surfaces are shown in Tables VII to XIII.

Examination of Table VII reveals the fact that 38 plants, which were immune, or nearly immune, from rust in the field, were V or IV for spike form. It is shown by Table VIII that a total of 81 plants, or nearly a third of the random group, were highly rust resistant, and ranked as V or IV in spike compactness. In Table IX there are 53 plants located in the squares denoting *dicoccum*-like rust resistance combined with *vulgare*-like stem cavity. Tables X, XI, and XII show similar results, the numbers of immune or near-immune plants with V or IV rachis articulation, rachis width and rachis hairiness being 45, 68 and 55, respectively. Table XIII shows that 20 plants which were classified as D or ID for rust reaction were V or IV for seed character. In each of the relationships between field rust reaction and morphological characters a substantial proportion of the plants showed desired combinations of resistance and the *vulgare*-like expression of the morphological character.

Relationships involving other characters than rust reaction were also studied. Spike form is a character in which the species *dicoccum* and *vulgare* differ markedly. In Table XIV the correlation of this character with each of the others is shown. The correlation coefficients that exceed three times their probable errors run from .20 to .37. On the whole they are distinctly higher than those given in Table VI. In fact only four of them are as low as, or lower than, the highest correlation between stem rust reaction and a morphological character. Yet the highest coefficient, .37, could hardly be said to represent a strong relationship.

TABLE VII  
RELATIONSHIP BETWEEN FIELD RUST  
REACTION AND SPIKE FORM IN  
VERNAL  $\times$  MARQUIS  $F_2$

		Spike form					
		D	ID	I	IV	V	
Field rust reaction	D	76	51	57	24	4	212
	ID	11	7	9	9	1	37
	I	2	4	5		1	12
	IV	1	2	4	3		10
	V	1	1		1	2	5
		91	65	75	37	8	276
		$r_{xy} = .19 \pm .039$					

TABLE VIII  
RELATIONSHIP BETWEEN FIELD RUST  
REACTION AND SPIKE COMPACTNESS  
IN VERNAL  $\times$  MARQUIS  $F_2$

		Spike compactness					
		D	ID	I	IV	V	
Field rust reaction	D	91	32	24	26	39	212
	ID	13	7	1	1	15	37
	I	3	1	3	2	3	12
	IV		3	2	1	4	10
	V	1	1	1		2	5
		108	44	31	30	63	276
		$r_{xy} = .16 \pm .030$					

TABLE IX  
RELATIONSHIP BETWEEN FIELD RUST  
REACTION AND STEM HOLLOWNESS  
IN VERNAL  $\times$  MARQUIS  $F_2$

		Stem hollowness					
		D	ID	I	IV	V	
Field rust reaction	D	60	59	53	25	15	212
	ID	6	8	10	11	2	37
	I	3	1	4	3	1	12
	IV		2	2	4	2	10
	V	1	1	1		2	5
		70	71	70	43	22	276
		$r_{xy} = .21 \pm .039$					

TABLE X  
RELATIONSHIP BETWEEN FIELD RUST  
REACTION AND RACHIS ARTICULATION  
IN VERNAL  $\times$  MARQUIS  $F_2$

		Rachis articulation					
		D	ID	I	IV	V	
Field rust reaction	D	48	57	74	26	7	212
	ID	9	5	11	8	4	37
	I	2	1	3	4	2	12
	IV	2	3	1	3	1	10
	V		1	1	2	1	5
		61	67	90	43	15	276
		$r_{xy} = .19 \pm .039$					

TABLE XI  
RELATIONSHIP BETWEEN FIELD RUST  
REACTION AND RACHIS WIDTH IN  
VERNAL  $\times$  MARQUIS  $F_2$

		Rachis width					
		D	ID	I	IV	V	
Field rust reaction	D	47	54	60	31	20	212
	ID	3	5	12	9	8	37
	I	1	2	6	1	2	12
	IV		1	2	2	5	10
	V	1	1	1		2	5
		52	63	81	43	37	276

$$r_{xy} = .24 \pm .038$$

TABLE XII  
RELATIONSHIP BETWEEN FIELD RUST  
REACTION AND RACHIS HAIRINESS  
IN VERNAL  $\times$  MARQUIS  $F_2$

		Rachis hairiness					
		D	ID	I	IV	V	
Field rust reaction	D	98	41	27	28	18	212
	ID	14	9	5	3	6	37
	I	4	3	2	1	2	12
	IV		3	1	4	2	10
	V	1				4	5
		117	56	35	36	32	276

$$r_{xy} = .24 \pm .038$$

TABLE XIII  
RELATIONSHIP BETWEEN FIELD RUST  
REACTION AND SEED CHARACTER  
IN VERNAL  $\times$  MARQUIS  $F_2$

		Seed character					
		D	ID	I	IV	V	
Field rust reaction	D	72	51	34	12	1	170
	ID	10	9	3	3	4	29
	I	1	3	4	1	1	10
	IV	1	2	3	3		9
	V		2		2		4
		84	67	44	21	6	222

$$r_{xy} = .27 \pm .042$$

TABLE XIV  
RELATIONSHIPS BETWEEN VARIOUS  
IMPORTANT MORPHOLOGICAL CHARACTERS  
IN THE  $F_2$  OF THE CROSS  
VERNAL  $\times$  MARQUIS

Characters associated	Coefficient of correlation	
Spike form and spike compactness	.34 $\pm$	.036
Spike form and stem hollowiness	.37 $\pm$	.035
Spike form and rachis articulation	.27 $\pm$	.038
Spike form and spikelet adherence	.31 $\pm$	.037
Spike form and rachis width	.29 $\pm$	.037
Spike form and stem thickness	.30 $\pm$	.037
Spike form and glume adherence	.32 $\pm$	.036
Spike form and rachis hairiness	.20 $\pm$	.039
Spike form and shoulder width	.06 $\pm$	.037
Spike form and shoulder shape	.26 $\pm$	.040
Spike form and glume shape	.23 $\pm$	.039
Spike form and keel sharpness	.52 $\pm$	.034
Spike form and awning	.08 $\pm$	.037
Spike form and seed character	.31 $\pm$	.041
Rachis articulation and glume adherence	.26 $\pm$	.038
Rachis articulation and rachis width	.11 $\pm$	.040

In addition to the relationships just discussed, various others were studied but no important correlations were found. Two examples, taken at random, are shown at the bottom of Table XIV.

### Field Rust Reaction

Field rust reaction is of primary importance in this study. Under the light epidemic conditions of 1928, although the two leading forms of 1927, forms 21 and 36, were present again, Marquis was much less heavily infected and slightly less uniformly infected than in 1927. Vernal did not have a trace of rust.

Sixty-four of the random group of  $F_2$  plants showed rust infection and 212 were completely resistant like Vernal. The results are given in Table V, line 1. Harrington and Smith (1) working with a similar cross, found that a single main factor governed the field rust reaction in 1927. In consideration of this, the fact that 212 of the  $F_2$  in 1928 were highly resistant and the remaining 64 more or less infected, appears to be significant. The same rust forms predominated in 1927 as in 1928, and it seems probable that the 3:1 ratio of non-infected to infected plants in 1928 indicates again the operation of a single main genetic factor.

### Discussion

A study of relationships involving field rust reaction and 15 morphologic characters was made on the cross Vernal (*T.dicoccum*)  $\times$  Marquis (*T.vulgare*). Perhaps the most outstanding feature of this work is its contribution to the knowledge of the possible character combinations which may result from crosses between wheat species having different numbers of chromosomes.

#### *Proportion of Vulgare-like Segregates*

Emphasis has been placed by several writers on the fewness of *vulgare*-like plants in *dicoccum*  $\times$  *vulgare* crosses. Thompson and Hollingshead (12) found only one *vulgare*-like plant in a *dicoccum*  $\times$  *vulgare*  $F_2$  of 210 plants. In the study by Harrington and Smith (1) similar results were obtained. (The random group of 276  $F_2$  plants in the present study contained three *vulgare*-like plants.) The present study, however, was not limited to a small random group, for it was evident that a large number of *vulgare*-like plants could only be expected from a very large population. Many thousands of  $F_2$  plants were grown and the expectation was fulfilled in the finding of 232 highly rust resistant plants of *vulgare* type. Having attained this result it is important to examine it in the light of previous work, and with respect to the general possibilities of wide species crosses in wheat improvement.

#### *Rôle of "Extra" Vulgare Chromosomes*

A first consideration is that of the significance of the seven "extra" pairs of *vulgare* chromosomes with respect to characters ordinarily found in *vulgare* varieties. The present study has furnished abundant evidence that *vulgare*-like plants may be *dicoccum*-like in rust reaction or in any one of 15 morphologic characters, and these 15 characters include practically all of those usually referred to as "species differentiating". In Table II containing the results concerning the first 85 plants of the random group, examples of such combinations of characters may be found. Attention has already been directed to several of them. The results also show many *dicoccum*-like plants that are *vulgare*-like in one or more of the 15 characters used. In addition, there occurred in the random sample many plants having about as many characters in the *dicoccum* or intermediate *dicoccum* condition as in the *vulgare* or intermediate *vulgare* condition. The results show that plants, having various combinations of *dicoccum* and *vulgare* characters, may be both vigorous and fertile,

and therefore that they probably have a fairly well balanced number of chromosomes. Cytological studies made by various investigators have shown that such plants have usually either 14 or 21 pairs of chromosomes or else closely approach one of those conditions. It would appear, then, that the seven "extra" *vulgare* chromosomes are not very exclusively concerned with *vulgare* characters.

The results given in the present study are supported by evidence from various sources, for the rôle played by the "extra" chromosomes has engaged the attention of many investigators. The literature on the subject is illuminating. Cytologists cannot distinguish between *vulgare* and *dicoccum* chromosomes. There is no direct proof that the same 14 *vulgare* chromosomes consistently mate with *dicoccum* chromosomes, or conversely, neither is there direct proof that the same seven chromosomes of *vulgare* usually fail to mate with *dicoccum* chromosomes. Available evidence indicates that *vulgare* characters are not necessarily associated with these chromosomes, nor are non-*vulgare* characters always found outside the 42-chromosome wheats. Some of this evidence may be reviewed briefly here. (a) Thompson (10) in his study of a *durum*  $\times$  *vulgare* cross, found that the 28-chromosome hybrids showed a few *vulgare* characters and the 42-chromosome hybrids had some *durum* characters, "even the most characteristic ones". (b) Thompson and Hollingshead (12) found that "the possession of one to four univalents in addition to the 14 bivalents did not make the characters of the plant more *vulgare*-like than those of some which had no univalents". They also state that characters which distinguish most *dicoccum* forms from *vulgare*, such as the nature of the keel and the thickness of the stem, are seen frequently in the 28-chromosome plants and cannot therefore be determined by the seven *vulgare* chromosomes. (c) *T. spelta*, a 42-chromosome wheat possesses a brittle rachis and tightly adherent glumes, two features that are very characteristic of *dicoccum*, and, as Watkins (15) points out, rachis brittleness is absent from *persicum*, a typical 28-chromosome species. (d) Watkins (15) in working with the "species differentiating" character keel (in cross-section) found that it could be transferred reciprocally between *turgidum* and *vulgare* by crossing. He believed that the normal confinement of a character to one species is no guarantee that it cannot be transferred by crossing. (e) Both Sax (8) and Kihara (4) state that in the crosses *durum*  $\times$  *vulgare* and *polonicum*  $\times$  *spelta* the  $F_2$  plants possessing 28 chromosomes reproduce the morphologic type of the tetraploid parent species, and that the  $F_2$  plants with 42 chromosomes reproduce the morphologic type of the hexaploid parental species. Malinowski (6) came to a similar conclusion with respect to the crosses *dicoccum*  $\times$  *vulgare* and *polonicum*  $\times$  *vulgare*. (f) Malinowski (6) pointed out that the existence of *dicoccum* varieties both susceptible and resistant to rust indicates that the causes of resistance do not depend upon the number of chromosomes but upon the genetic constitution of particular varieties. (g) Sapehin (7), who has done an immense amount of genetical and cytological work on *durum*  $\times$  *vulgare* crosses, denies that there are such things as individual species differentiating characters. Vavilov (13) appears to take the same stand.



The results obtained in the present study, together with the evidence cited from other work shows that whatever the exact importance of the seven "extra" *vulgare* chromosomes may be, these chromosomes are far less *exclusively* concerned with the usual *vulgare* condition of morphologic characters and rust reaction than is generally supposed.

#### *Character Relationships*

The second consideration is that of the genetic relationships between the various characters of the species concerned. In crosses between wheats having different numbers of chromosomes great difficulty is experienced in obtaining precise combinations of characters from both species. Results from various studies differ according to the species and varieties that have been used, but, in general, failure to secure certain combinations may be attributed to the use of far too few hybrid plants. Sax's (8) doubt as to the possibility of transferring *durum* rust resistance to *vulgare* by means of crossing appears to have been due largely to the small size of the population he studied. On the other hand Hayes, Stakman and Aamodt (2), working with a large population, found that *durum* resistance *could* be transferred to *vulgare*, but the resistance so transferred was not as strong as in the *durum* parent variety used. Thompson (10), in 1925, obtained similar results. Harrington and Smith (1) working with a large population proved that the resistance of Vernal emmer could be transferred to *vulgare*.

Vavilov (13) states that the immunity of *T. persicum* to leaf rust and downy mildew is not connected with distinct morphologic characters, but he remarks also that there appears to be a general connection between morphologic type and rust reaction.

Sapehin (7) found, in his very extensive study of a *durum* × *vulgare* cross, that many characters of the *vulgare* parent had been transmitted to the *durum*-like hybrid types. He states that these types exist in the homozygous condition, have perfect fertility, and that cytological examination of 165 plants representing the principal types showed balanced sets of 28 chromosomes in each.

In a study of intercrosses among the species *vulgare*, *turgidum* and *spelta*, Watkins (14) found that the characters keel sharpness, glume adherence and rachis articulation, were important in differentiating species, and that they were closely associated. Thompson and Hollingshead (12) in their *dicoccum* × *vulgare* study did not find these characters especially closely associated. In the present work it has been shown (Table VI) that glume adherence and keel sharpness are not correlated with field rust reaction, and that rachis articulation is only weakly associated with the field rust expression. It was also shown (Table XIV) that none of these three characters are correlated at all strongly with spike form, an important character for distinguishing between *dicoccum* and *vulgare*.

Thompson and Hollingshead (12) in their study of a cross between Marquis and the *dicoccum* variety *farrum* (Perc.) considered six characters, of the 20 used, to be of species differentiating importance. They observed that the



great majority of individual plants were *dicoccum*-like in these six characters. It was therefore expected by the writer that the present investigation, being on a similar cross, would show similar results. The results for the six characters in question appear in the third, fourth, fifth, sixth, eighth and last columns of Table II. It is apparent from the results that no strong association of these characters or of any two of them was found. There are, however, some weak relationships indicated. The lack of agreement between the Thompson and Hollingshead result and those of the present study appears to be due to a difference in the *dicoccum* varieties used.

The most important feature of the present study was the lack of any strong or even moderately strong relationships between field rust reaction and morphologic characters. The results from the random sample give abundant evidence of this, as shown particularly in Tables II, IV and VI to XIII. Consistent with this was the occurrence, in the entire  $F_2$  population of 21,480 plants, of 232 plants which were immune from rust in the field, yet *vulgare*-like in nearly all characters. It was particularly interesting that the few *dicoccum* resemblances that existed in the 232 plants appeared to be distributed at random.

It would seem that the chief difficulty in the way of obtaining a desired combination of characters from a cross between a 28-chromosome and a 42-chromosome wheat is that of getting a sufficiently large progeny. Various combinations of characters have been obtained from nearly all such studies depending largely upon the size of population. The smaller the population the fewer were the desirable combinations obtained. Rust resistance and the important morphologic characters frequently referred to as "species differentiating" have proved no exception to this statement. Probably differences in the genetic constitutions of different varieties are much more important in species crosses than is generally believed.

#### *Mendelian Inheritance*

It has been pointed out by Sax (8), Malinowski (6), Kihara (4), Thompson (10), Vavilov (13), Watkins (14), and others that, in crosses between wheat species having different chromosome numbers, genetic analysis of the results is unreliable because of the great mortality due to various types of sterility. The work of Watkins (14) and Thompson and Cameron (11) indicate that a large part of the zygotic mortality in a cross such as Vernal  $\times$  Marquis is due to faulty endosperm development. Zygotic elimination has also been shown by Sax (8), Kihara (4), Thompson (10), and others to result from irregular distribution of the chromosomes. Again, it may be due to the genetic constitution of the embryo, although this has not been proved.

There are, then, several possible causes for the uneven  $F_2$  distribution but the extent and nature of their interference with the course of Mendelian inheritance are largely unknown. Whatever these effects may be they apparently do not altogether interfere with Mendelian ratios. Watkins (15) in his study of *turgidum*  $\times$  *vulgare* ( $F_2$ ) states, "It is clear that some pairs of characters

show Mendelian inheritance". Harrington and Smith (1) in the cross Vernal  $\times$  Marquis found simple Mendelian ratios with respect to two distinct factors governing seedling reaction to rust. Their results, which were confirmed by those of the present study, also showed a 3:1 ratio with respect to field rust reaction. Later Smith and Harrington (9) reported the occurrence of three main factors for the inhibition of chlorophyll development in the cross Vernal  $\times$  Marquis.

In view of the evidence presented there would seem to be much to gain and little to lose by the application of Mendelian principles to the results from a wide species cross. Clear-cut Mendelian ratios have occurred for several characters, and these characters were selected for their interest to the investigators rather than with respect to Mendelian inheritance. It is reasonable to assume that Mendelian ratios will be found for many other characters in crosses between wheat species of different chromosome number.

#### *Economic Breeding Considerations*

Combinations of Vernal resistance with the Marquis expression of some morphologic characters were found very infrequently in the "random" group of 276  $F_2$  plants. These characters are spike form, rachis articulation and seed character. If the *exact* expressions of various characters exhibited by the parental varieties were essential in a new hybrid variety, the chances of obtaining Vernal rust resistance in combination with *all* of the characters of Marquis excepting its rust susceptibility would be very small even from an  $F_2$  population of 100,000 plants. Fortunately this is not the case. It is not at all essential to obtain a close likeness to Marquis for such morphologic characters as spike form, spike compactness, stem hollowness, rachis width, stem thickness, rachis hairiness, shoulder width, glume shape, kee' sharpness and awning. In fact, it would be desirable that a new variety differ distinctly from Marquis and from other commonly grown varieties in several outward features in order that it might be easily recognizable.

There are, however, several *dicoccum* or near-*dicoccum* characters that are distinctly *not* wanted. Two of these are the easy articulation of the rachis and the tight adherence of the glumes, the former because of the importance of the spikes remaining intact on the straw before threshing, and the latter on account of the necessity of the seed coming free from the chaff in threshing. Seed character may be added here in so far as it is related to milling and baking quality. Tables X and XIII show that approximately 12% and 6% respectively, of random sample plants classified as "D" for field rust reaction were in the V and IV classes for rachis articulation and seed character. If the ID class for rust reaction be accepted as satisfactorily resistant, the proportions of desirable plants rise to about 15% and 9% respectively. Since glume adherence, showed no significant relationship with rust reaction it need not be considered here. It is easily seen that a population of over 20,000 plants may be no more than enough to furnish a few hundred promising individuals.

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## THE EFFECT OF THE ULTRA-VIOLET COMPONENT OF THE SUN'S RADIATION UPON SOME AQUATIC ORGANISMS<sup>1</sup>

BY A. BROOKER KLUGH<sup>2</sup>

### Abstract

Specimens of three species of fresh-water entomostracans—*Daphnia pulex*, *Daphnia magna* and *Cypris reticulata*—were each exposed to sunlight which had passed through filters which transmitted different regions of the solar spectrum. One filter ("Total") transmitted both visible and ultra-violet radiation, a second ("Novial") transmitted the visible only and a third ("U.V.") transmitted only the ultra-violet. By prolonged exposure the animals were killed under the Total and U.V. filters, while under the Novial they lived indefinitely. The chief point of interest lies in the comparison of the results obtained with these entomostracans which live in shallow pools with the results of previous experiments (2) on three marine entomostracans which remain at a considerable depth in the sea when the illumination is at all intense; the comparison shows that the former have a far greater resistance to the lethal effects of the sun's ultra-violet radiation. Developing embryos of the squid, *Loligo pealii*, were experimented upon in a similar manner; these embryos, which are enclosed in a gelatinous matrix attached to large algae in the intertidal zone, and, at low tide, are exposed to full sunlight, were extremely resistant to ultra-violet radiation.

The research work reported upon in this paper is a continuation of that done in 1927 (2) and was carried on at the Atlantic Biological Station in 1928. It includes not only some marine organisms but also some fresh-water species. The apparatus employed and the experimental procedure were the same as that described in the previous paper, with the exception that as no animals which required a low water temperature were used there was no necessity to bring the water through the copper coil immersed in a mixture of ice and salt. In these experiments species of entomostracans placed in tubes were exposed to sunlight passed through various filters transmitting different regions of the solar spectrum.

### Experiments on *Daphnia pulex*

- July 7, 1928. 3 *D. pulex* set in each tube at 10.30 a.m. Pyrheliometer (Py.) reading—1.30 gm. cal. per cm<sup>2</sup> per minute. Water temperature 17° C.  
 12.00 noon. Py 1.40. Temp. 19° C. All normal.  
 7.00 p.m. Bright sun all afternoon. Temp. 19° C. All normal.  
 July 8. 10.30 a.m. Bright sun. Temp. 19° C. All normal.  
 2.00 p.m. Py. 1.19. Temp. 17° C. All normal.  
 7.00 p.m. Bright sun all afternoon. All normal.  
 July 9. 10.30 a.m. Py. 1.26. Temp. 16°.

Total (i.e. under the filter which transmits both ultra-violet and visible radiation) two dead.

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Under the other two filters (i.e. under the visible only [Novial] and ultra-violet filters) normal.

12 noon. Py. 1.34. Temp. 16° C.

3.00 p.m. Py. 1.26. Temp. 16° C.

July 10. 10.30 a.m. Under total filter—All dead. Under other filters—All normal.

July 10. 3 *D. pulex* set in each at 10.30 a.m. Fog in morning, sun from 12.30 on, Py. 0.97.

July 11. Fog in morning. Sun from 12.30 a.m. on, Py. 1.19. All normal.

July 12. Fog in morning. Sun from 11. a.m. on, Py. 1.15. All normal.

July 13. Fog in morning. Clouds and faint sun all day. All normal.

July 14. Rain all day. All normal.

July 15. Sun and heavy clouds all day. All normal.

July 16. Fog in morning. Sun rest of the day.

7.00 p.m. T. (Total)—Two dead. U.V.—All dead. N. (Novial)—All normal.

July 17. Sun till 12.30 a.m. Py. 1.28 - 1.34. Heavy clouds rest of day. Same as on 16th.

July 18. Faint sun most of the day. Condition of animals the same as on 16th.

July 10. 9.00 a.m. T.—All dead. U.V.—All dead. N.—All normal and two young.

July 21. 3 *D. pulex* set in each tube at 9.30 a.m.

July 22. Bright sun in morning, cloudy from noon on.

2 p.m. T.—One dead. U.V.—Normal. N.—Normal.

July 23. Rain all day.

July 24. 10. a.m. T.—All dead. U.V.—All normal. N.—All normal.

July 24. Cloudy till 4 p.m., then bright sun till evening.

July 25. Sun till 1.45 p.m. Py. 1.17 - 1.19. Animals as on July 24.

July 26. Sun all day. Py. 1.38 - 1.52.

8.00 p.m. T.—All dead. U.V.—All dead. N.—One dead. Two alive, active, and three young.

#### *Experiments on Cypris reticulata.*

July 10. 3 *C. reticulata* set in each tube at 10.30 a.m. Fog in morning. Sun from 12.30 p.m. on.

July 11. Fog in morning. Sun from 12.30 p.m. on. Py. 1.19. All normal.

July 12. Fog in morning. Sun from 11.00 a.m. on. Py. 1.15. All normal.

July 13. Fog in morning. Clouds and faint sun all day. All normal.

July 14. Rain all day. All normal.

July 15. Sun and heavy clouds all day. All normal.

July 16. Fog in morning. Faint sun rest of the day.

7.00 p.m. T.—One dead. U.V.—Normal. N.—Normal.

- July 17. Sun till 12.30 p.m. Py. 1.23 - 1.34. Heavy clouds rest of the day. Animals same as on 16th.
- July 18. Faint sun most of the day. Condition of animals as on the 16th.
- July 19. 9.00 a.m. T.—All dead. U.V.—One dead. N.—All normal.
- July 18. 3 *C. reticulata* set in each tube at 5.55 p.m.
- July 19. Fog in morning. Sun from noon on. Py. 1.25. All normal.
- July 21. Sun all day. Py. 1.07 - 1.34. All normal.
- July 22. Bright sun in morning, cloudy from noon.
- July 23. Rain all day.
- July 24. 10.00 a.m. T.—Two dead. U.V.—Normal. N.—Normal.
- July 24. Cloudy till 4 p.m., then bright sun.
- July 25. Sun until 1.45 p.m. Py 1.17 - 1.19. No change in animals.
- July 26. Sun all day. Py. 1.38 - 1.52.
- July 27. 10.00 a.m. Cloudy all day. T.—All dead. U.V.—One dead. N.—All normal.
- July 28. Sun in morning; rain from 11.00 a.m. on.
- July 29. Fog till noon, sun rest of day.
- July 30. Sun till 4.30 p.m. Py. 1.19 - 1.32.
- July 31. Bright sun till noon with clouds. Py. 1.32. Faint sun from noon on. 7.00 p.m. T.—All dead. U.V.—Two dead. N.—One dead.

*Experiments on Daphnia magna.*

- July 26. 3 *D. magna* set in each tube at 5.00 p.m.
- July 27. Cloudy. All normal.
- July 28. Sun in morning, rain from 11 a.m. on. All normal.
- July 29. Fog till noon, then sun. All normal.
- July 30. Sun till 4.30 p.m., then rain, then sun from 6.30 p.m. on. Py. 1.19 - 1.32. All normal.
- July 31. Bright sun till noon, with cumulus clouds and cirrus haze. Py. 1.32. Faint sun rest of day. Normal.
- Aug. 1. Bright sun with cirrus clouds till noon. Faint sun on. Normal.
- Aug. 2. 9 a.m. T.—Two dead. U.V.—All normal. N.—All normal.
- Aug. 3. Rain and fog in morning.  
2 p.m. T.—All dead. U.V.—All dead. N.—All normal.
- Aug. 3. 3 *D. magna* set in each tube at 2.30 p.m. Faint sun in afternoon and evening.
- Aug. 4. Rain and then cloudy all day. Normal.
- Aug. 5. Rain and fog all day. Normal.
- Aug. 6. Bright sun and perfectly clear all day. Py. 1.26 - 1.34.
- Aug. 7. Bright sun with cirrus and cirro-cumulus clouds all day. Py. 1.17 - 1.26.  
7.00 p.m. T.—All dead. U.V.—All dead. N.—All normal.



*Experiments on the developing eggs of Loligo pealii.*

Before giving the data concerning these experiments it is necessary to define the stages in development which are recognized and numbered. A study of the developing eggs of this species showed that there were six stages which could be recognized by examination with a hand lens. These states, and the figures which correspond to them in the monograph by Brooks (1880), are as follows:

- Stage 1. Early blastula. Brooks' Fig. 1.
- Stage 2. Late blastula. Brooks' Fig. 3.
- Stage 3. Embryo becoming "flask-shaped". Brooks' Fig. 7.
- Stage 4. Embryo showing constriction between head and body. Brooks' Fig. 9.
- Stage 5. Embryo more constricted. Eye-stalk prominent. Brooks' Fig. 12.
- Stage 6. Eye-stalks, and projections, which later become the arms, prominent. Brooks' Fig. 13.

July 31. Three eggs in Stg. 1 and three in Stg. 5 set in each tube at 11.20 a.m.

Bright sun with cumulus clouds till noon, faint sun from noon on.

Aug. 1. Bright sun with cumulus clouds till noon, faint sun rest of day.

All normal.

Aug. 2. All normal.

Aug. 3. Fog and rain in morning.

2.00 p.m. T.—One egg set in Stg. 1 dead, all eggs set in Stg. 5 dead.

U.V.—Two eggs set in Stg. 1 dead, all set in Stg. 5 dead. N.—All normal.

Aug. 4. Rain, and then cloudy, all day.

Aug. 5. Rain and fog all day.

Aug. 6. Bright sun and perfectly clear all day. Py. 1.26 - 1.34.

Aug. 7. 9.45 a.m. T.—All dead. U.V.—All dead. N.—All normal.

Eggs set in Stg. 1 had gone to Stg. 4 and those set in Stg. 5 had gone to Stg. 6.

Aug. 7. Three eggs in Stg. 2 and three eggs in Stg. 4 set in each tube at

9.45 a.m. Bright sun with cirrus and cirro-cumulus clouds all day. Py.

1.17 - 1.26. Temp. 14° C.

Aug. 8. Rain all day.

Aug. 9. Rain all day.

Aug. 10. Fog and light rain all day.

T.—All set in Stg. 2 gone to Stg. 3. All set in Stg. 4 still Stg. 4.

U.V.—All set in Stg. 2 gone to Stg. 3. One set in Stg. 4 still Stg. 4. Two set in Stg. 4 now between Stg. 4 and 5.

N.—All set in Stg. 2 now Stg. 3. Two set in Stg. 4 now Stg. 5. One set in Stg. 4 now Stg. 6.

Aug. 11. Rain all day. Temp. 14° C.



- Aug. 12. Perfectly clear and bright sun all day. Py. 1.26 - 1.36. Temp. 14° C.
- Aug. 13. Bright sun with cirrus haze all day. Py. 0.84 - 1.03.
- Aug. 14. Bright sun all day. Py. 1.19. Temp. 14 - 15° C.
- Aug. 15. 10.00 a.m.  
T.—All set in Stg. 2 dead in Stg. 3. All set in Stg. 4 dead in Stg. 4.  
U.V.—All set in Stg. 2 dead in Stg. 3. One set in Stg. 2 dead in Stg. 3.  
Two set in Stg. 4 dead in Stg. 5.  
N.—One set in Stg. 2 dead in Stg. 3. Two set in Stg. 2 alive in Stg. 4.  
All set in Stg. 4 alive in Stg. 6.
- Aug. 7. Ten eggs in Stg. 1, and ten in Stg. 2, set in each tube at 7.30 p.m.  
For weather record from Aug. 8 to 14, see record of the previous experiment.
- Aug. 10. T.—All set in Stg. 1 now Stg. 2. All set in Stg. 2 now Stg. 4.  
U.V.—One set in Stg. 1 dead, the rest between Stg. 2 and 3. All set in Stg. 2 now Stg. 4.  
N.—All set in Stg. 1 now between Stg. 3 and 4. All set in Stg. 2 and Stg. 5.
- Aug. 15. Bright sun all day. Py. 1.09 - 1.26. Temp. 15° C.
- Aug. 16. Bright sun with a few cumulus clouds all day. Py. 1.13 - 1.32.  
7.00 p.m. T.—All set in Stg. 1 dead in Stg. 2 to 3. All set in Stg. 2 dead in Stg. 4 to 5.  
U.V.—One set in Stg. 1 dead in Stg. 1, rest dead in Stg. 3. All set in Stg. 2 dead in Stg. 4 to 5.  
N.—One set in Stg. 1 dead in Stg. 3, rest alive and in Stg. 5. All set in Stg. 2 alive in Stg. 6.

### Discussion

The three species of entomostracans experimented upon, *Daphnia pulex*, *Daphnia magna* and *Cypris reticulata*, are fresh-water species which occur in pools and the chief interest in the results obtained lies in a comparison of these results with those derived from experiments upon three species of entomostracans reported upon in the previous paper. These three species, *Calanous finmarchicus*, *Tortanus discaudatus*, and *Eurytemora herdmanni*, remain at a considerable depth in the sea when the illumination is at all intense, and come to the surface only on the darkest nights. The average time of exposure to sunshine taken to kill all the animals of the first-mentioned species under the "Total" and the "U.V." filters was 36 hours, the average time for the second species was 16.5 hours, and for the third species it was 16 hours. The much higher resistance to ultra-violet radiation of the fresh-water species is shown by the fact that the average time for *D. pulex* was 104 hours, for *D. magna* 61 hours and for *C. reticulata* 192 hours. The results show, however, that while these latter species are resistant to a moderate amount of ultra-violet they can be killed by an overdose.

The eggs of the squid, *Loligo pealii*, are enclosed in a copious gelatinous matrix and are attached in bunches to the larger marine algae, such as *Ascophyllum nodosum*, in the intertidal zone. They are consequently at times exposed to the ultra-violet radiation from the sun and it was not to be expected that they would be particularly sensitive to short wave-length radiation. This supposition was borne out by the experiments, but it was found that they were killed by long exposure to ultra-violet light.

#### Acknowledgment

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THE PENETRATION OF WATER VAPOR INTO WOOD<sup>1</sup>BY L. M. PIDGEON<sup>2</sup> AND O. MAASS<sup>3</sup>

## Abstract

The rate of diffusion of water vapor through wood has been studied through a comparison of the time taken for samples of various thickness to become saturated. This process is, in a sense, the converse of natural drying, and for comparative purposes is more amenable to careful control of pressure and temperature. Continuous measurements of the amount of adsorption were carried out by the use of a quartz spring balance completely enclosed in the apparatus at a constant vapor pressure.

Comparative numerical values have been obtained of the rate of diffusion of water vapor through spruce (*Picea canadensis*) and pine (*Pinus banksiana*) in various directions, through heartwood and sapwood, and through samples of different lengths. The results are considered as evidence that the movement of water through wood at concentrations below the saturation point, takes place as vapor diffusion through the spaces of the wood structure due to the pressure gradient consequent on the difference of moisture content.

In a previous paper <sup>\*</sup>(1) measurements of the adsorption of water by wood were described. This paper deals with an extension of the original method which affords a comparative means of measuring the rate of diffusion of aqueous vapor through wood. By this means the rate of penetration of vapor through different woods in various directions may be compared.

A knowledge of the manner by which hygroscopic moisture moves through wood is both theoretically and practically interesting as it is intimately connected with problems of drying. Stillwell (3) has investigated the diffusion of water vapor through a sample of wood the opposite ends of which were held in equilibrium at different relative humidities. In this way the movement of water vapor through wood was measured when the steady state had been attained. The present work more nearly approximates the conditions of natural drying. It is, in fact, the reverse of drying carried out under conditions which may be regulated carefully and under which the rate of the process may be determined.

Since wood is a substance of complicated structure the adsorption of a vapor will consist of two factors: first, the penetration of the adsorbate into the wood structure, and second, the actual adsorption of the vapor on the walls of this internal structure. In much of the previous work on the subject the existence of two factors has been overlooked. In the present investigation an attempt has been made to separate them. A brief description of wood structure will exemplify the method.

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<sup>\*</sup>The experimental procedure in the paper referred to and the work described in it, as well as in this paper, had been completed before June, 1929

In the coniferous woods, to which attention has been confined, there are no continuous longitudinal passages through the tree as are common in the hardwoods. Hence the passage of liquids and gases in this direction must take place through the fibres themselves. These fibres or tracheids vary in length from 0.5 mm. to 10.0 mm. having in spruce an average 3.5 mm. (Sutermeister). Communication between the fibres is established by means of the bordered pits, i.e., apertures containing the valve-like torus. In the heartwood it is assumed that this flap is glued to one side by the deposition of resins thus accounting for the impenetrability of this part of the tree.

It will be evident that in a sample where the longitudinal dimension is considerably less than the average length of a fibre, every tracheid will be cut through at least once so that all the walls of the wood structure will be immediately accessible to an entering vapor. That is, if a vapor suddenly surrounds such a sample, the apparent rate of adsorption will correspond to the true rate for the gas—solid interface in question. The wood structure (microscopic) will have no influence on the rate of adsorption.

If now a larger sample in which the longitudinal direction is considerably greater than the length of one fibre is taken, the entering vapor must pass through such passages as exist in the wood to reach the inner fibres (3). Thus by comparing the time to saturation of such a sample with that of the standard where the wood structure plays no part, a comparative measure of the rate of diffusion of the vapor through wood is obtained. This constitutes a valuable method to compare different woods and different parts of the same wood.

Since wood is an anisotropic substance the rate of penetration in the three directions, longitudinal, radial, and tangential, will not be the same. These rates have been examined by masking the required faces to restrict the flow to the desired directions.

### Experimental

The apparatus employed is similar to that described previously, consisting essentially of a quartz spring balance from which the sample is suspended. This is enclosed in a glass chamber which is immersed in a glass-sided thermostat constant to  $\pm .01^\circ \text{C}$ . The tube is connected to a manometer, a tube of phosphoric anhydride, and a water tube to supply vapor to the sample. The whole apparatus was evacuated by means of a mercury condensation pump backed by a Hyvac pump. Deflections of the spiral were noted by means of a cathetometer and the corresponding weight found from the constant for the spiral. Changes in weight corresponding to 0.1% of the total could be detected with samples weighing from 0.2 to 0.3 gm.

The sample is dried by long evacuation in the presence of phosphoric anhydride. It has been found that a constant reproducible value may be obtained by evacuation at ordinary temperatures for 12 hr. The value so obtained is considered as the dry weight, and the percentage increase due to

(3) This neglects the possibility of passage of vapor to the inner fibres by solution in the wood substance.

adsorption of water vapor is calculated on this basis. A constant vapor pressure of water is maintained in the apparatus by controlling the temperature of a water surface in communication with the sample. The rate of adsorption is found by noting the increase of weight with time under constant conditions of temperature and pressure. A constant weight is reached at the saturation point. In practice the spirals were mounted in triplicate so that three samples could be subjected to identical conditions.

### Samples

Coniferous woods only have been examined and in particular spruce (*Picea canadensis*) and jack pine (*Pinus banksiana*). The wood was freshly cut and dipped in paraffin to preserve the original condition. A sample of air dried spruce was also investigated.

The logs were cut transversely with a fine circular saw the thickness varying from 1.5 mm. to 20 mm. From these the actual samples were cut and suspended from the quartz spiral by means of a fine silver wire. The desired faces such as radial, tangential, transverse, etc., were blocked off with paraffin. The weight of stirrup and paraffin was found before the experiment and subtracted from the weight as calculated by the deflection of the spiral. A blank run showed that paraffin does not adsorb water vapor to a sufficient extent to interfere with gravimetric measurements, a fact which had been noticed previously. (4)

### Standards

To separate the effect of thickness on vapor diffusion, as mentioned above, it was necessary to know the time to saturation of a free surface. Against this was compared the saturation time for thicker samples where complete saturation may only be attained by penetration of the vapor through the wood structure. A sample of 1.5 mm. in the longitudinal direction was chosen as the standard sample. This length being greatly less than that of the average fibre every fibre was cut through at least once, so that every surface was immediately accessible to an entering vapor. This was confirmed by the fact that the time to saturation was the same for finely ground wood meal in which the wood structure had been largely destroyed.

At a given temperature and pressure the time required to reach saturation was fairly constant among various samples of standard thickness. Table I exemplifies this.

TABLE I  
TIME TO REACH SATURATION

Spruce No.	Time in minutes				Average
	2	4	6	9	
Sapwood	18.0	20.0	21.5	26.0	21.2
Heartwood	21.0	17.5	21.5	—	20.0

It will be noticed that heartwood and sapwood adsorb at the same rate when structural differences are removed.

The theoretical aspect of this process has been discussed previously. At this point it is necessary only to assume that this time is that required to saturate a free surface when exposed directly to the vapor, and that any extension of the time in thicker samples will be due to the structure of the wood.

It is essential that the various samples be exposed to a constant vapor pressure in every case. The most convenient way to attain this result was to immerse the water tube in a stirred mixture of melting ice, and all the samples discussed in this paper have been examined at a vapor pressure of 4.58 mm. of mercury and at a temperature of 23° C.

#### Method of Comparison

It was necessary to find some convenient basis of comparison of the diffusion rates for different samples; as in many cases the saturation point was reached only after long exposure to the water vapor. It was therefore assumed that all samples of the same wood would finally attain the saturation value reached by the standard, were the experiment protracted until equilibrium was completely established. This assumption has been tested in the case of samples which are saturated in a reasonable length of time and it has been found to be valid. Hence if the saturation value is measured or assumed, it is possible to utilize the time to half-value as a comparative measure of rate. This greatly reduces the time in the case of very thick samples.

#### Discussion of Results

##### Longitudinal diffusion

##### SPRUCE (*Picea canadensis*)

Samples with a longitudinal dimension of 5, 9, 14, and 20 mm. have been examined both in the case of heartwood and sapwood. These results are

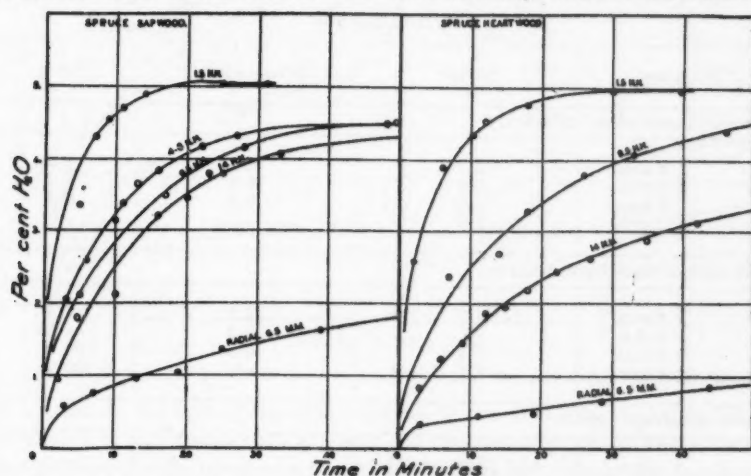


FIG. 1. Rate of penetration of water vapor into spruce wood, longitudinally and radially.



plotted in Fig. 1. The remarkable difference between the two kinds of wood is at once apparent. The sapwood represents a very open condition as even in the 14 mm. sample which must be three or more fibre lengths, the rate compares favorably with the standard. So that in spruce sapwood the passages between the fibres do not offer great resistance to an entering vapor. The case is quite different for heartwood. For the standard sample of 1.5 mm. thickness the rate is similar to that for sapwood, so that the difference in the thicker samples must be due to the resistance offered to the entering vapors by the stopped up openings between the fibres. The marked difference between the rates of diffusion in the two kinds of wood is also shown by a consideration of the time to half-value as indicated in Table II. Since a small change in  $T/2$  corresponds to a very great difference in rate, the differences are apparently reduced by this method of comparison.

The results of time experiments on various samples of air-dried spruce are not essentially different from those of the green wood as indicated in Table II. This fact is of interest as this wood had aged in the open for an indefinite period. From the point of view of vapor penetration, long weathering has little effect; the heartwood and sapwood remain in their initial condition.

#### *Radial Diffusion*

The result of a typical experiment on the rate of diffusion in the radial direction is plotted in Fig. 1. A greater difference between the two kinds of wood is manifested than in the longitudinal direction. Also the rate is very much slower, in fact in the case of heartwood, after the first rapid adsorption which

TABLE II  
TIME OF DIFFUSION TO HALF-VALUE OF SATURATION

T/2 in minutes			
Thickness	Spruce	Spruce (dried)	Pine
Sapwood (Longitudinal diffusion)			
1.5 mm.	2.3	2.2	2.2
5.0 mm.	4.3	4.4	4.2
9.5 mm.	6.4	4.5	6.6
14.0 mm.	8.0	—	—
Heartwood (Longitudinal diffusion)			
1.5 mm.	2.0	2.1	2.5
5.0 mm.	—	5.5	4.0
9.5 mm.	9.9	10.4	50.0
14.0 mm.	18.0	—	100.0
(Radial diffusion)—Spruce			
6.5 mm.	310 (Heartwood) 122 (Sapwood)		



saturates all the readily accessible surfaces, the adsorption proceeds so slowly that even the time to half-value must be obtained by extrapolation. The magnitude of these values is indicated in Table II.

Diffusion in the radial direction must take place through the medullary rays which are comparatively few in number. Communication between the rays and the fibres which make up the bulk of the wood substance is established by means of the pits. This in the case of heartwood, where these openings are partially stopped in some way, the wood is almost impenetrable to the vapor.

The great time taken for diffusion in the radial direction where there are few natural openings lends validity to the assumption that water vapor passes only through the channels in the wood, and when these are non-existent the vapor cannot diffuse into the inner fibres. This is of interest in view of the suggestion (2) that hygroscopic moisture passes through wood by a process of alternate condensation and vaporization by which it crosses the open spaces as a vapor and condenses on the cell walls to be dissolved in them as a liquid. A repetition of this process was suggested as the mechanism of diffusion.

#### Longitudinal diffusion PINE (*Pinus banxiana*)

Experiments similar to those on spruce were performed on pine; a typical set of results are listed in Table II and plotted in Fig. 2. As before a standard sample was examined and the rate compared with the thicker samples. It is evident that the time required for saturation of a sample of 1.5 mm. thickness is exactly the same as for spruce. This would be expected at a vapor pressure

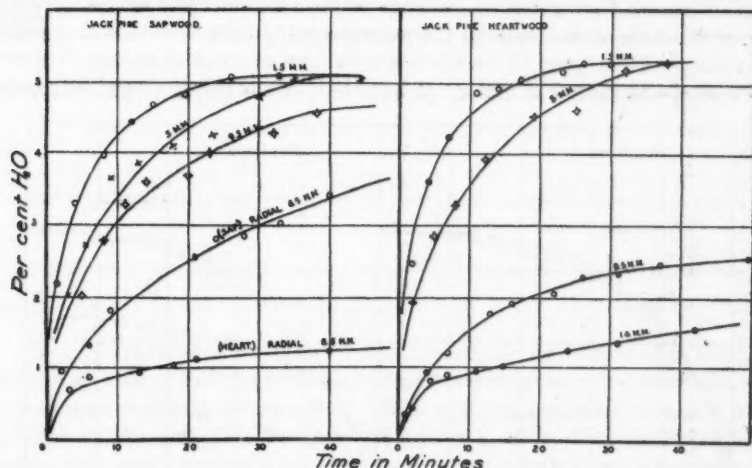


FIG. 2. Rate of penetration of water vapor in jack pine wood, longitudinally and radially.

of 4.5 mm. in the light of the results and discussion set forth previously (1). In this work it was found that at lower relative vapor pressures the adsorption isothermals of different woods tended to coincide, and only in the region of the saturation pressure were large differences noted.

The values for sapwood show a marked similarity to those of spruce indicating a similar condition of porosity. In the case of heartwood, however, there is considerable difference, while the 5 mm. sample is similar (it will be seen in the next section that in this sample nearly all the fibres are open) the thicker samples appear quite as impenetrable to longitudinal diffusion as the radial sections of spruce. It is thus apparent that the natural processes which produce heartwood from sapwood result in a much greater stopping of the pores in this wood. This is perhaps to be expected in view of the higher resin content of pine.

### Radial Diffusion

An examination of the curves representing diffusion indicates that pine is in general more penetrable in this direction than spruce. The rate for sapwood is somewhat greater and that for heartwood is the same as that for spruce, while from a consideration of the longitudinal penetration it should be much slower.

### Number of Effective Fibre-lengths per Sample

In order to give the results of time measurements a meaning in terms of wood structure, it is necessary to find the number of fibre ends which must be passed to saturate each sample completely.

The length of the fibre is not constant so that an average value must be taken. According to Sutermeister the average for spruce is 3.53 mm. If this value is accepted, a sample whose longitudinal dimension is 5 mm. should contain at least one fibre-length on the average and, if both ends of such a sample are open the larger part of the fibres will be open at one end at least. If now, one end of the sample is closed, at least half of the fibres should be masked

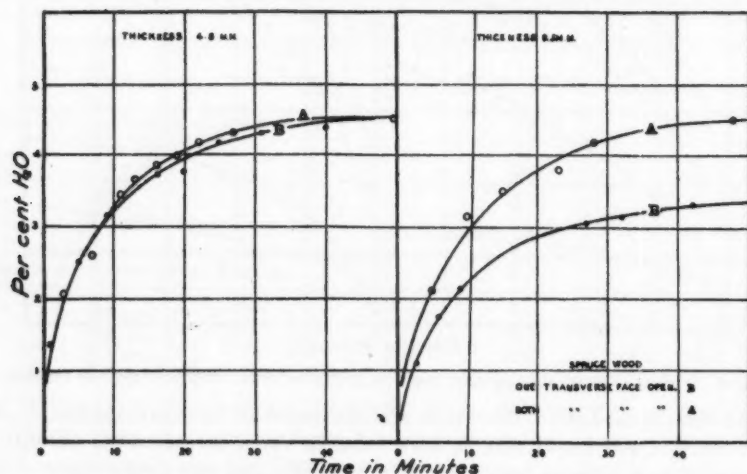


FIG. 3. Effect of the fibre length on the rate of penetration of water vapor in spruce wood.

so that they must be reached through the pores connecting them to fibres whose cut end is open. In Fig. 3 the time curves are indicated for the same samples with first both and later one transverse face open. It will be seen that in the case of the 5 mm. sample there is little change in diffusion rate when one face is blocked. Apparently in a sample of this thickness with one transverse end closed most of the fibres are open at the other face indicating a fibre-length greater than 5 mm.

In the case of a sample of 9.5 mm. length considerable difference is noticed when one end is blocked. It would appear that in this section at least one fibre on the average is so placed that it may be reached only through the openings between the fibres. Hence in this sample the closing of one of the transverse ends brings another set of fibre-ends into play causing a proportionate retardation in the rate of saturation.

The effect of closing one of the transverse faces in the case of a number of samples is indicated in Table III.

TABLE III  
RATE OF DIFFUSION OF WATER VAPOR IN WOOD

T/2 in minutes			
Thickness in mm.		One face open	Two faces open
Spruce			
Sapwood	4.5	4.4	4.3
	9.5	2.2	6.4
	14.0	11.5	8.0
Pine			
Sapwood	5.0	5.0	4.2
	9.5	7.4	6.6
Heartwood	5.0	19.7	4.0
	9.5	200.0	50.0
	14.0	?	160.0

The table illustrates well the extreme impermeability of pine heartwood. It is to be concluded that the formation of heartwood in this wood involves almost a complete stopping of the pores. This stopping, whether it is due to the binding to one side of the torus which acts as a valve, or to the deposition of resins, etc., is of a very gas-tight nature as there is little penetration even with considerable difference of pressure.

In pine the effective fibre-length is shorter than in spruce, as closing the end of a 5 mm. sample caused an increase in the time to half-value. This is particularly noticeable in the case of heartwood, indicating that the closing of the end isolated another set of fibres from direct contact with the entering vapors.

### Discussion of the Mechanism of Diffusion Through Wood

At any given temperature and pressure there is an equilibrium amount of water adsorbed on wood. (Neglecting hysteresis effects (1).) Hence a dry surface exposed to a constant vapor pressure of water will adsorb until this equilibrium value is reached. In the case of the thicker samples under discussion, the rapid adsorption by the outer fibres will remove water from the fine capillaries, and will tend to maintain the pressure gradient which is initially established across the openings between the fibres when the vapor first surrounds the dried wood. As the fibres become saturated the vapor pressure of adsorbed water increases and the pressure gradient decreases; hence the rate of diffusion falls to zero as complete saturation is attained throughout the sample. This behavior is exhibited by the time curves for the thicker samples. Since the time required to saturate the elementary surface is comparatively short, the shape of the curve in these cases is due to the diffusion of vapor from fibre to fibre under the influence of a decreasing pressure head.

This mechanism assumes that all movement of moisture below the fibre saturation point takes place in the vapor state through the open spaces in the wood structure. The movement of water from a point of higher concentration to a point of lower is simply due to the higher vapor pressure in the former case, and to the fact that essentially open passages may be found through the wood structure.

It is, of course, conceivable that in a complex substance like cellulose with many hydroxyl groups, water may move by some combination of solution followed by evaporation across the open spaces. However, as mentioned above, the extreme slowness of diffusion in directions in which there are few natural openings coupled with the fact that openings between the fibres do exist (gases and liquids may be forced through wood with varying degrees of ease) would tend to rule out this possibility as a major effect.

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## THE EFFECT OF LOW TEMPERATURES UPON THE IMPACT RESISTANCE OF STEEL CASTINGS<sup>1</sup>

By R. W. MOFFATT<sup>2</sup>

### Abstract

The investigation deals with the effect of low temperatures on the impact resistance of steel castings and forgings. Low, medium and high carbon steel castings and a few alloys of vanadium, nickel, and vanadium-nickel steel castings were examined. The metals were subjected to low temperatures, both before and after heat treatment. The temperatures for the tests varied from room temperatures to temperatures well below 0° F., so as to extend below the ordinary atmospheric range of temperatures found in northern climates.

It was found that the impact resistances of the metals decreased for temperatures below the freezing point. For specimens, not heat treated, the impact resistance at -40° F. may be only one-third to one-half of that at room temperature. Heat treatment increases the impact resistance at room temperatures and temperatures below the freezing point. The impact resistance at -40° F. for the heat-treated metal compared favorably with the impact resistance of the untreated metal at room temperature, 68° F. Heat treatment may slightly lower the yield point and the ultimate tensile strength, but it increases the ductility and the impact resistance of the metal. By proper heat treatment of steel castings the impact resistance at -40° F. may be brought over 300% higher than that of the untreated metal at that temperature.

### Introduction

From information gained from several sources, it appears that the percentages of broken connecting rods, car wheels, car axles, and various steel castings, are higher during the winter months, especially during December and January. Just why this is so does not seem to be clearly known. It may be due to poor or improper design, poor lubrication in cold weather, defective materials, or changes in the physical properties of the metals, at temperatures below the freezing point. It is suggested that any one of these causes, or their combinations, may be responsible for failures in the metal.

Until recent years, very little has been known about changes that take place when metals are subjected to temperatures other than normal. A number of investigations and interesting experiments have been made to determine the effect of temperature upon the structure and physical properties of the metal.

As early as 1837, Sir William Fairbairn (2) made a number of experiments with cast iron at various temperatures. In 1871 Peter Spence (7) carried out a number of investigations with cast iron at low temperatures. Between 1885 and 1905, a great deal of attention was given the subject of testing metals at various temperatures, especially at elevated temperatures. F. C. Langenberg (4) at Watertown Arsenal made impact tests at various temperatures from -80° F. to 1000° F. The results of his investigations are to be found in the papers *An Investigation of Behavior of Certain Steels Under Impact Tests at Different Temperatures*, published in the *Journal of the Iron and Steel Institute*; *Carnegie Scholarship Memoirs* 1923, and *Investigation on the Influence of Temperature on the Charpy Impact Value of a Group of Steels of*

<sup>1</sup> Manuscript received April 4, 1930.

Contribution from the laboratories of the University of Manitoba, Winnipeg, Manitoba with financial assistance from the National Research Council.

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Varying Composition, Transactions of American Iron and Steel Institute, 1923. Langenberg, Reinhold (6), Charpy (1), Guillet (3), Yamada (8), and others have contributed valuable information. A great number of their experiments have been with various steels and alloys of steels, such as low and medium carbon steels, nickel-chromium steel, and chrome-vanadium steel, the range of temperatures extending beyond ordinary atmospheric temperatures. Very little concise information can be found on impact tests on steel castings within ordinary atmospheric temperatures, say  $-50^{\circ}$  F. to  $150^{\circ}$  F.

A complete review of the present state of knowledge of the properties of metals at various temperatures, and a discussion of the necessity for promoting further knowledge is given in a pamphlet issued by the American Society of Mechanical Engineers and the American Society for Testing Materials entitled, Symposium on Effect of Temperature upon the Properties of Metals.

### Experimental Work

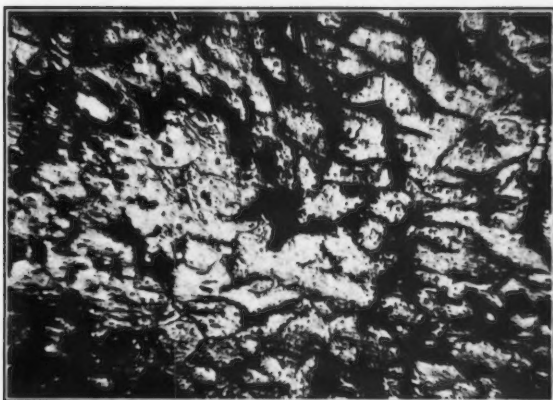
The bar specimens used for the impact tests were 0.385 in. square and 3 in. long, with a  $45^{\circ}$  V-notch  $1\frac{1}{8}$  in. from one end, the depth of the notch being 0.13 in. The exact angle and depth of the notch was obtained by means of a standard steel templet. A Rhiehle (pendulum type) impact testing machine was used to break the specimens, four specimens being tested at each temperature, and the average taken. Temperatures of test bars were confined to a range between  $-70^{\circ}$  F. and  $150^{\circ}$  F. The low temperatures were obtained by immersing the test bars in a bath of carbon dioxide snow and acetone. A Dewar silvered vacuum tube was used for a container for the bath and test bars. The apparatus was placed as conveniently near the impact testing machine as possible, and each specimen transferred quickly to the machine. To obtain the change in temperature in transferring the specimens, a low temperature thermometer was inserted in a hole drilled in a dummy specimen. The cross-section of the dummy was in the form of a cross and of such dimensions as to give a temperature rise corresponding to an actual specimen. The dummy and thermometer were placed in the cooling bath, and a check thermometer placed in the cooling medium. A gauge was used in placing the specimens in the impact testing machine, and the time taken in transferring the specimen from the bath to the machine was observed by means of a stop watch. The time required was only 5 to 10 sec., and very little effect was noted on the impact resistance. Even 10 to 20 sec. to effect the transfer of the specimen did not affect the results materially.

For convenience the investigation was divided into three parts:

1. The determination of the effect of temperatures below freezing point upon the strength of steel castings subjected to impact.
2. The determination of the effect of chemical composition upon the strength of steel castings subjected to impact at temperatures below freezing point.
3. The determination of the effect of heat treatment upon the strength of steel castings subjected to impact at temperatures below freezing point.



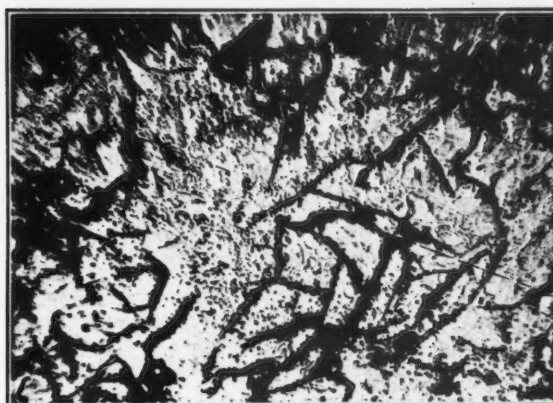
PLATE I



No. 3. *Ordinary cupola grey cast iron.*  $\times 100$ .



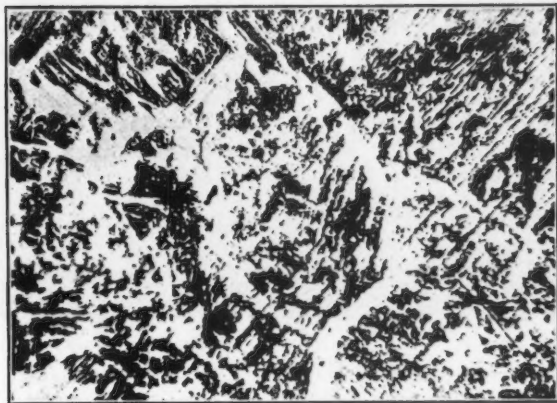
No. 2. *High silicon cupola grey cast iron.*  $\times 100$ .



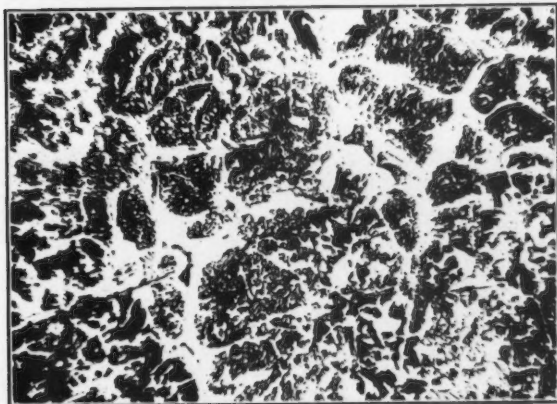
No. 1. *Electric furnace grey cast iron.*  $\times 100$ .



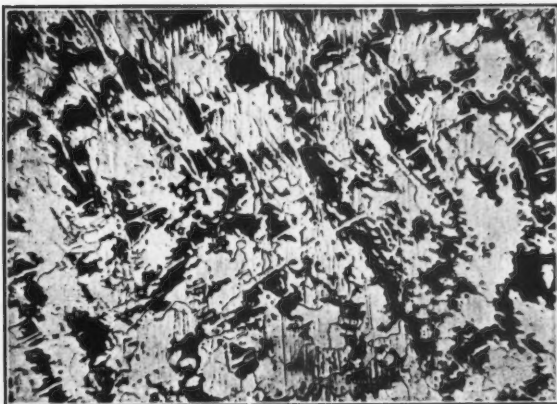
## PLATE II



No. 4. Ordinary electric furnace steel casting.  
×100.



No. 5. High carbon electric furnace steel casting.  
×100.



No. 6(a). Electric furnace steel casting. ×100.  
Heated to 1600° F. in 12 hr., held at  
1600° F. 2 1/4 hr., cooled in furnace  
to 1300° F., in air from 1300° F.

1. The first part of the paper is devoted to a general discussion of the problem of the existence of solutions of the system of equations

$$\begin{cases} \Delta u = f(x, y, z, u, v, w) \\ \Delta v = g(x, y, z, u, v, w) \\ \Delta w = h(x, y, z, u, v, w) \end{cases} \quad (1)$$

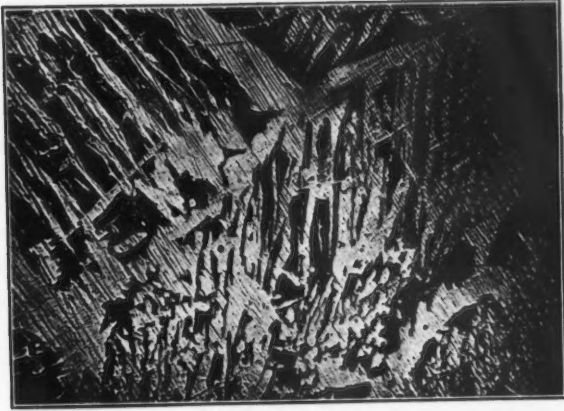
where  $f, g, h$  are functions of the coordinates  $x, y, z$  and the unknown functions  $u, v, w$ .

$$\begin{cases} \Delta u = f(x, y, z, u, v, w) \\ \Delta v = g(x, y, z, u, v, w) \\ \Delta w = h(x, y, z, u, v, w) \end{cases} \quad (2)$$

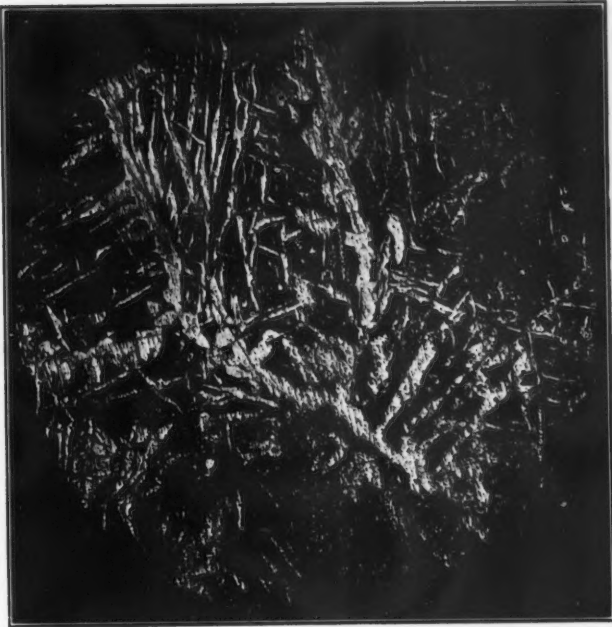
where  $f, g, h$  are functions of the coordinates  $x, y, z$  and the unknown functions  $u, v, w$ .

$$\begin{cases} \Delta u = f(x, y, z, u, v, w) \\ \Delta v = g(x, y, z, u, v, w) \\ \Delta w = h(x, y, z, u, v, w) \end{cases} \quad (3)$$

PLATE III



No. 7. *Electric furnace steel casting, as cast.*  
×100.



No. 7. *Electric furnace steel casting, as cast.* ×150.





The nature and scope of the work may be briefly outlined as the examination of,

1. Cast iron made in the electric furnace.
2. High silicon cupola cast iron.
3. Ordinary cupola cast iron.
4. Ordinary electric furnace cast steel.
5. High carbon electric furnace cast steel.
6. Electric furnace cast steel heat treated.
7. Electric furnace vanadium-steel as cast and heat treated.
8. Nickel-vanadium steel castings.
9. Vanadium-steel castings forged and heat treated.

(A) *Studies on Grey Cast Irons*

Three grey cast irons were studied; the chemical compositions are given in Table I, and the results of the tests in Table II. The values in each case are the average of four tests. While No. 2 was classified as high silicon cast iron, the percentage of silicon was less than for No. 1, the electric cast iron.

The results show a decrease in the impact resistance at the low temperatures, but the results are not very reliable owing to the low impact resistance of grey cast iron. The decrease may be due to other causes rather than to the freezing of the metal. The fractures of all the specimens had a blackish, coarsely crystalline appearance. The microphotographs show elongated and curved plates of graphite. Plates I, II and III show the microphotographs of these specimens.

TABLE I  
CHEMICAL COMPOSITION OF GREY IRONS

Specimen No.	Classification of material	Graphitic carbon per cent	Combined carbon per cent	Manganese per cent	Silicon per cent	Phosphorus per cent	Sulphur per cent
1	Electric furnace cast iron	2.18	0.76	0.61	3.01	0.616	0.099
2	High silicon cupola cast iron	2.22	0.94	0.46	2.73	0.592	0.110
3	Ordinary cupola cast iron	2.49	0.83	0.51	2.35	0.626	0.108

TABLE II  
RESULTS OF TESTS ON GREY CAST IRON

Specimen No.	Classification of material	Brinell number	Temperature of test in 0° F.	Impact resistance, in ft-pounds per sq. in.
1	Electric furnace cast iron	156	68	10
			-4	9
			-40	7.5
2	High silicon cast iron	162	-68	15
			-4	9
			-31	7
3	Ordinary cupola cast iron	196	68	18
			5	15
			-31	11

*(B) Plain Carbon Steel Castings*

The material selected for the plain carbon steel castings was supposed to be representative of material used in commercial castings. Table III gives the chemical composition and Table IV the results of the impact tests at the various temperatures.

TABLE III  
CHEMICAL COMPOSITION OF CARBON STEELS

Specimen No.	Classification of material	Combined carbon per cent	Silicon per cent	Man-ganese per cent	Phos-phorus per cent	Sulphur per cent
4	Ordinary electric furnace	0.29	0.24	0.45	0.032	0.044
5	High carbon electric furnace	0.43	0.28	0.55	0.035	0.048
6	Electric furnace	0.23	0.27	0.66	0.029	0.046
7	Same as No. 6	0.23	0.27	0.66	0.029	0.046

TABLE IV  
IMPACT TESTS ON PLAIN CARBON STEEL CASTINGS

Specimen No.	Classification of material	Brinell number	Temp. of test in ° F.	Impact resistance, in ft-pounds per sq. in.	Heat treatment
4	Ordinary electric furnace	127	70 -10 -25	148 48 43	As cast
5	High carbon electric furnace	149	68 10 -4 -25	64 37 29 26	As cast
7	Electric furnace cast steel	173	68 23 -4	135 85 43	As cast
6a	Electric furnace cast steel	149	68 23 -4	182 138 100	Heated to 1600° F. in 12.5 hr., held at 1600° F. for 2 hr. 20 min., cooled in furnace to 1300° F., then cooled in air from 1300° F.
6b	Electric furnace cast steel	—	68 0 -40	237 168 132	Heated to 1600° F., cooled in furnace to 1100° F., then cooled in air from 1100° F.
6c	Electric furnace cast steel	—	68 0 -40	203 158 130	Heated to 1600° F., cooled in furnace to 1250° F., then cooled in air from 1250° F.
6d	Electric furnace cast steel	—	68 0 -40	245 187 142	Heated to 1600° F., cooled in air; reheated to 1450° F., then cooled in air.
6e	Electric furnace cast steel	—	68 0 -40	336 249 183	Heated to 1600° F., quenched in water at 70° F., reheated to 1450° F., cooled in furnace to 1100° F., then cooled in air from 1100° F.

No. 4 specimens were classified as low carbon steel castings. The impact resistance was much higher than for the grey cast irons. There was, however, a remarkable decrease in the impact resistance at the low temperatures. Comparing the chemical analysis of No. 4 and No. 5, it will be noted that the carbon content of No. 5 is considerably higher than No. 4. The impact resistance of No. 5, the high carbon steel, is much lower than the low carbon No. 4. The specimens used for No. 6 and No. 7 series of experiments were taken from a fairly large casting, and the heat treatment of No. 6(a) was given in a commercial furnace. The other specimens of this series were heated in a laboratory muffle furnace.

All the specimens of No. 6 series were heated to 1600° F. The fractures of all the specimens showed a crystalline grain. The temperature of 1600° F. was either too low, or the specimens were not held at that temperature long enough to become thoroughly soaked. However, the fractures of No. 7 specimens, as cast, showed a much coarser grain than those of No. 6. The microphotographs No. 6(a) and No. 7 show clearly the grain, before and after heat treatment.

From an examination of the results of tests, it will be seen that the impact resistance of the heat treated specimens at low temperatures compare favorably with the impact resistance of the untreated specimens at room temperature, 68° F. The beneficial effect of heat treatment is quite noticeable especially at the low temperatures. The fractures of No. 6(e) showed the finest grain, and the impact resistances were higher at all temperatures for these water quenched specimens. The impact resistances of the specimens 6 (b) to 6(e) inclusive, tested at -40° F. are from 200% in the case of 6(c) to 325% in the case of 6(e) higher than No. 7 tested at -4° F. No. 6(a) shows a decrease of 45% in impact resistance from 68° F. to -4° F. No. 6(b) between the temperatures 68° F. and -40° F.

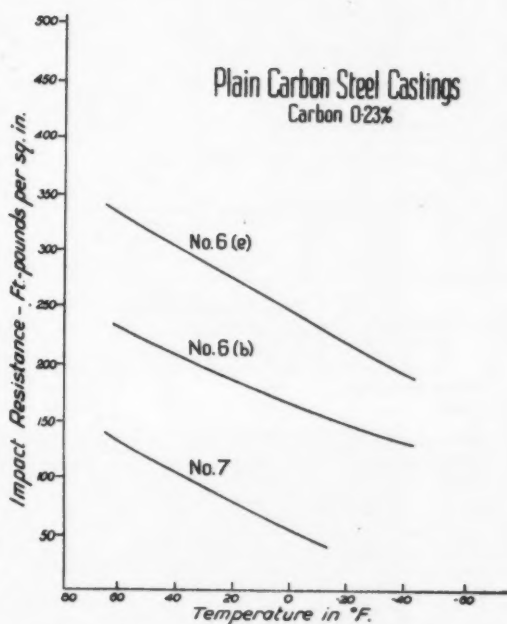


FIG. 1. Effect of low temperatures and heat treatment. No. 6(e), heated to 1600° F., quenched in water at 70° F., reheated to 1450° F., cooled in furnace to 1100° F., in air from 1100° F.; No. 6(b), heated to 1600° F., cooled in furnace to 1100° F., in air from 1100° F.; No. 7, as cast.

shows a decrease of 44%, No. 6(c) a decrease of 36%, No. 6(d) a decrease of 42%, No. 6(e) a decrease of 45.5%, No. 7 as cast, shows a decrease of 68% between the temperatures 68° F. and -4° F. The results of the above series are clearly shown in the accompanying graph (Fig. 1).

F. C. Langenberg (4) in his investigation (5) of steels under impact at different temperatures, found a decrease of impact resistance at the low temperatures. The decrease is probably not so marked in the steels investigated as that of the plain carbon steel castings.

### (C) Vanadium Steel Castings

The chemical compositions of the vanadium steel castings are given in Table V. The heat treatment, and the results of the impact tests at the various temperatures, are given in Table VI.

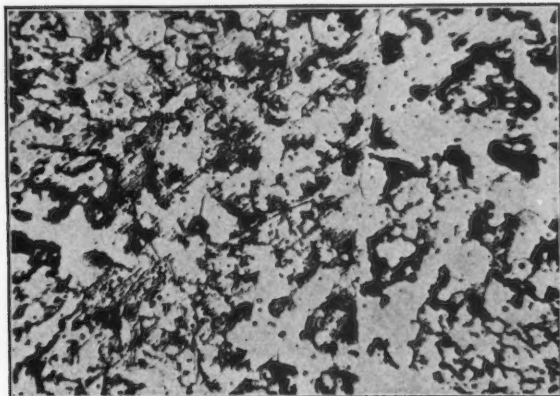
TABLE V  
CHEMICAL COMPOSITION OF VANADIUM STEEL CASTINGS

Specimen No.	Classification of material	Combined carbon	Silicon	Manganese	Sulphur	Phosphorus	Vanadium
8	Cast vanadium steel	0.23	0.32	0.53	0.050	0.043	0.22
10	Cast vanadium steel	0.25	0.27	0.64	0.062	0.033	0.19
11	Cast vanadium steel	0.25	0.27	0.64	0.062	0.033	0.19
12	Cast vanadium steel	0.23	0.22	0.60	0.048	0.035	0.188
13	Cast vanadium steel	0.27	0.31	0.67	0.048	0.036	0.20
14	Cast vanadium steel	0.27	0.36	0.66	0.049	0.039	0.20

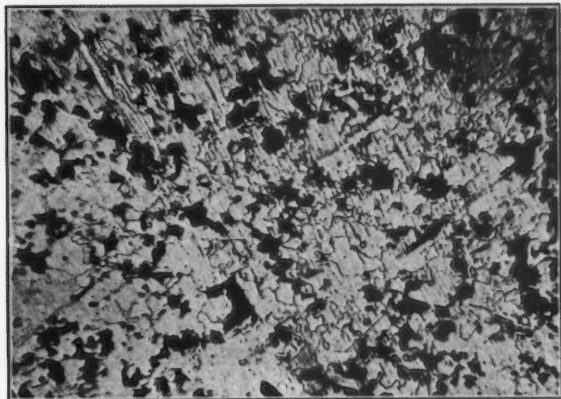
TABLE VI  
RESULTS OF TESTS ON VANADIUM STEEL CASTINGS

Specimen No.	Classification of material	Temp. of test in ° F.	Impact resistance, in ft-pounds per sq. in.	Heat treatment
8	Cast vanadium steel	69 -58	325 150	Heated to 1660° F. for 3 hr., cooled in furnace to 1100° F., and from 1100° F. cooled in air.
10	Cast vanadium steel	68 14 -9 -58	216 168 148 112	Heated 1660° F. for 3 hr., cooled in furnace to 1100° F., and from 1100° F. cooled in air.
11	Cast vanadium steel	70 21 -13 -58	46 31 26 20	As cast
12	Cast vanadium steel	70 -70	440 265	Heated to 1660° F. for 3 hr., cooled in furnace to 1100° F., and from 1100° F. cooled in air.
13	Cast vanadium steel	70 -70	499 320	As above for No. 12.
14	Cast vanadium steel	70 -70	326 173	As above for No. 12.

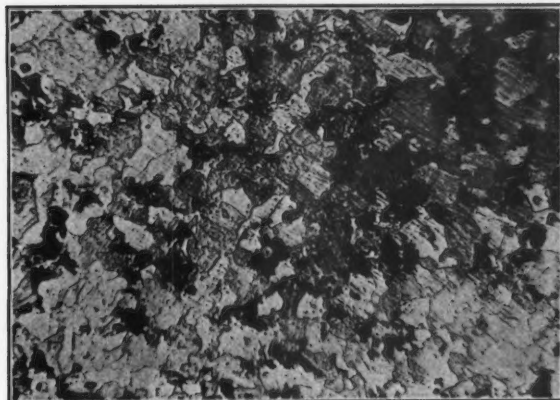
# PLATE IV



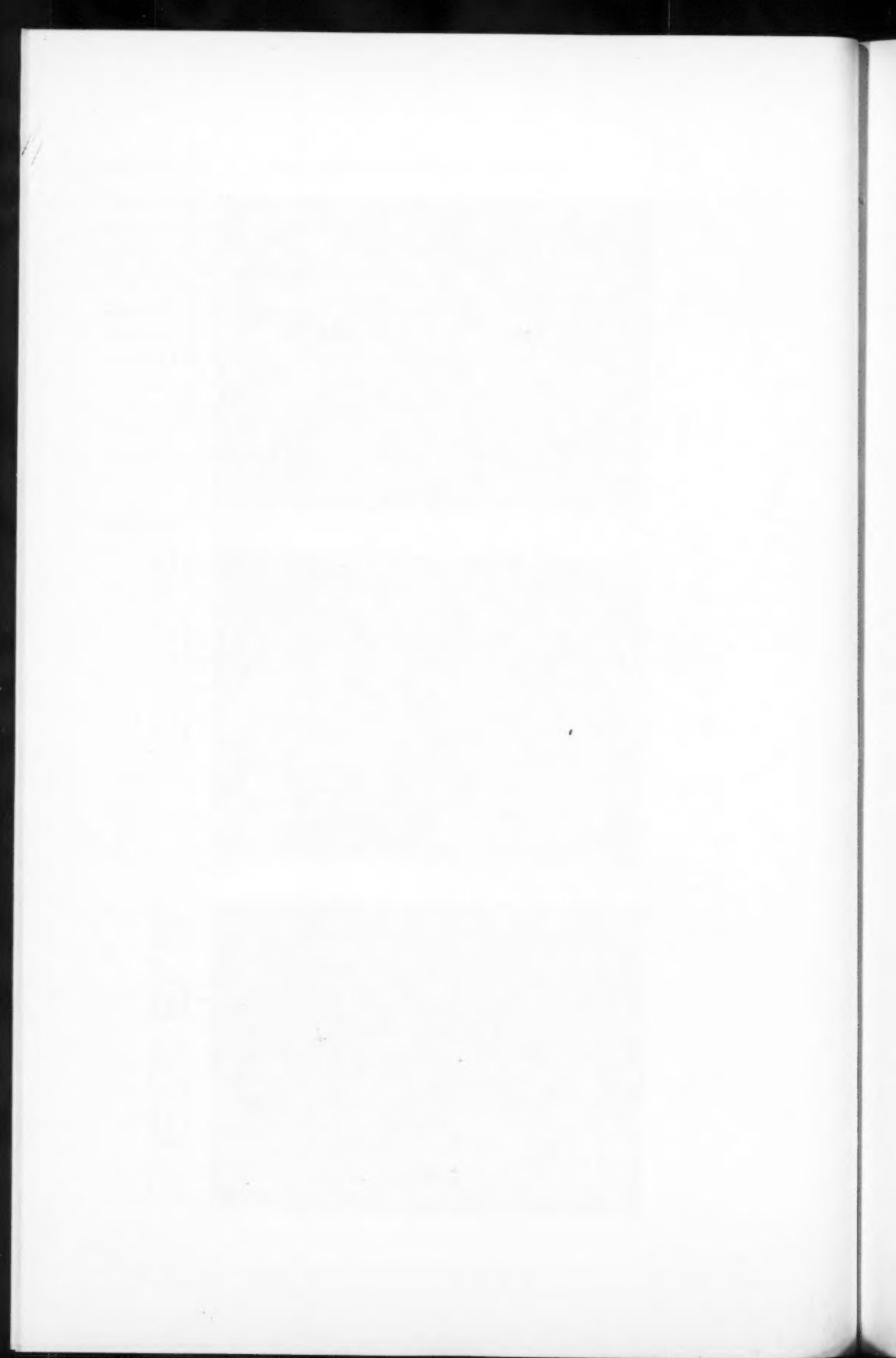
No. 11. Vanadium steel casting.  $\times 100$ . As cast.



No. 10. Vanadium steel casting.  $\times 100$ . Heated to  $1660^{\circ}\text{F.}$  for 3 hr., cooled in furnace to  $1100^{\circ}\text{F.}$ , in air from  $1100^{\circ}\text{F.}$



No. 8. Vanadium steel casting.  $\times 100$ . Heated to  $1660^{\circ}\text{F.}$  for 3 hr., cooled in furnace to  $1100^{\circ}\text{F.}$ , in air from  $1100^{\circ}\text{F.}$

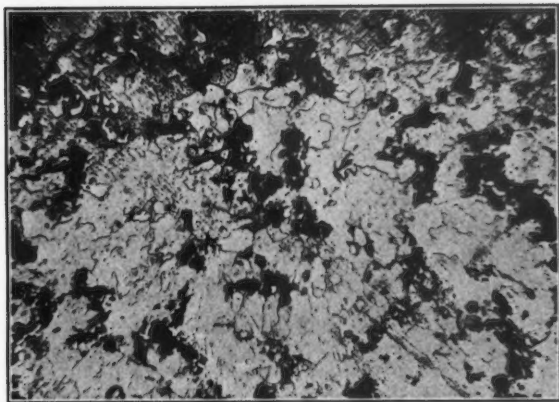




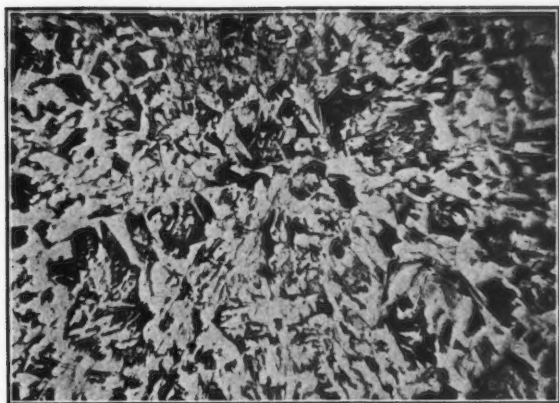
# PLATE V



No. 12. Vanadium steel casting.  $\times 100$ . Heated to  $1660^{\circ}\text{F.}$  for 3 hr., cooled in furnace to  $1100^{\circ}\text{F.}$ , and in air from  $1100^{\circ}\text{F.}$



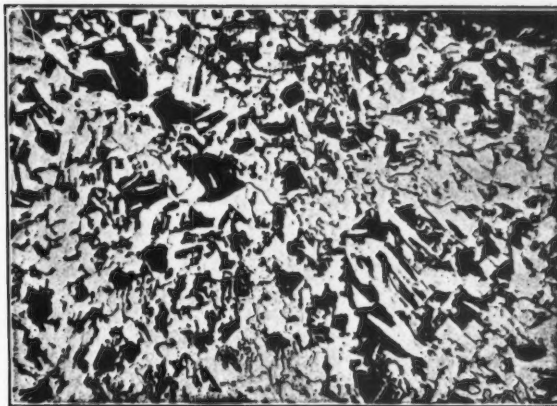
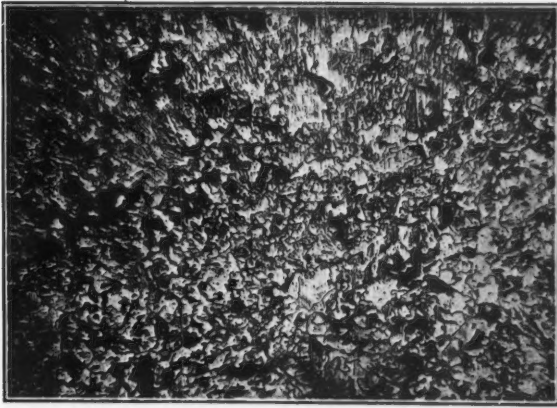
No. 13. Vanadium steel casting.  $\times 100$ . Heated to  $1660^{\circ}\text{F.}$  for 3 hr., cooled in furnace to  $1100^{\circ}\text{F.}$ , and in air from  $1100^{\circ}\text{F.}$



No. 14. Vanadium steel casting.  $\times 100$ . Heated to  $1660^{\circ}\text{F.}$  for 3 hr., cooled in furnace to  $1100^{\circ}\text{F.}$ , and in air from  $1100^{\circ}\text{F.}$



PLATE VI



No. 15, 16, 17. Nickel steel castings.  $\times 100$ . Heated to  $1750^{\circ}\text{F}$ . and cooled in air, reheated to  $1450^{\circ}\text{F}$ ., cooled in air from  $1450^{\circ}\text{F}$ .

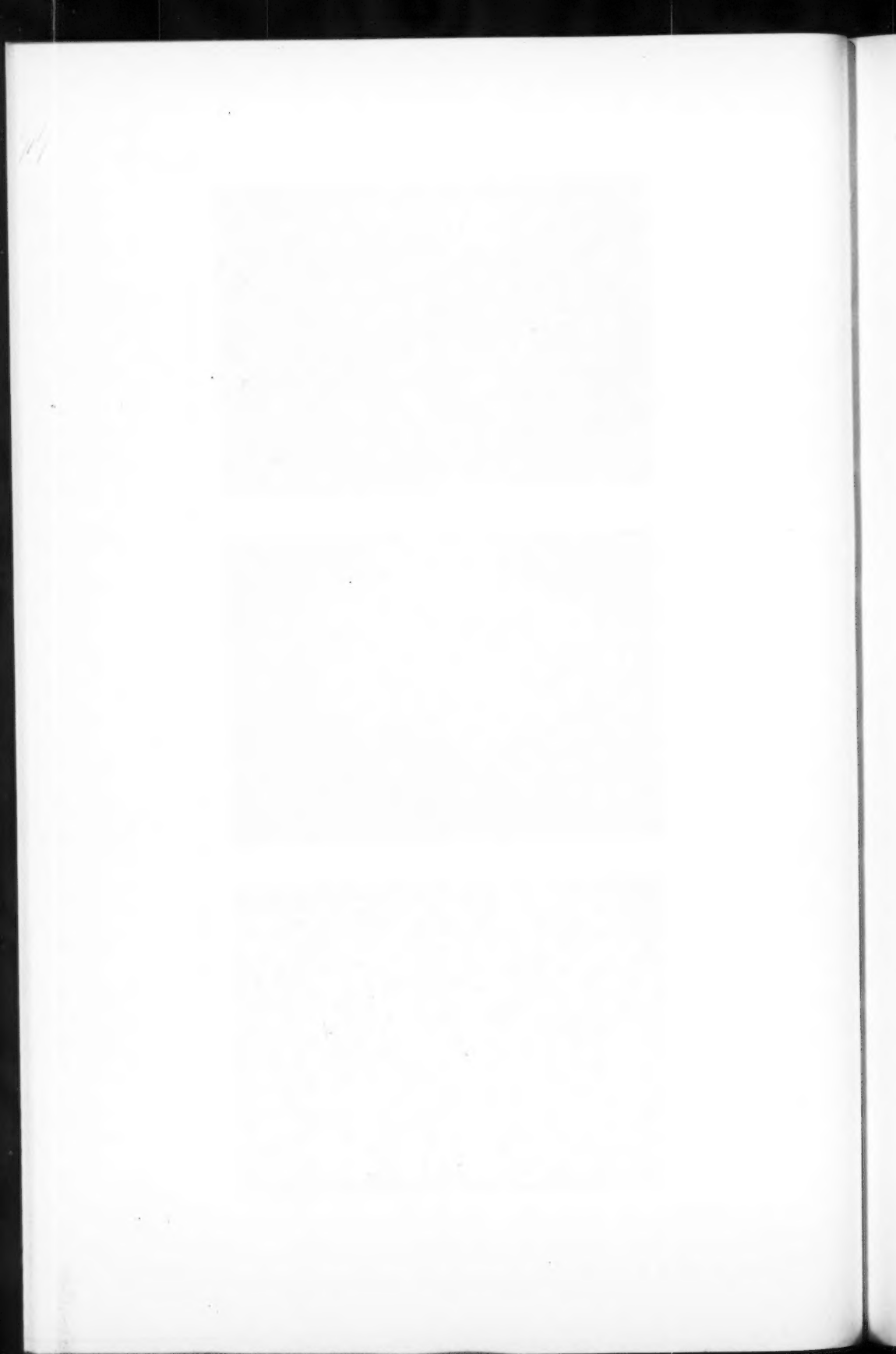
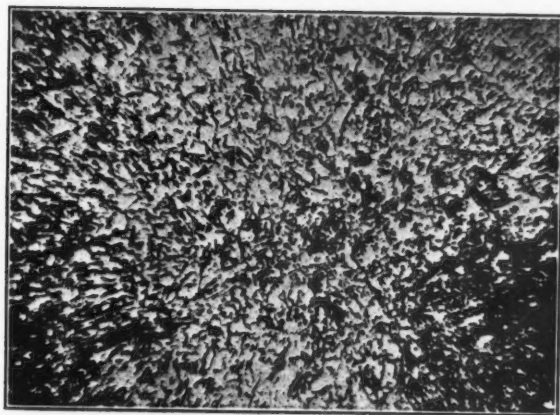
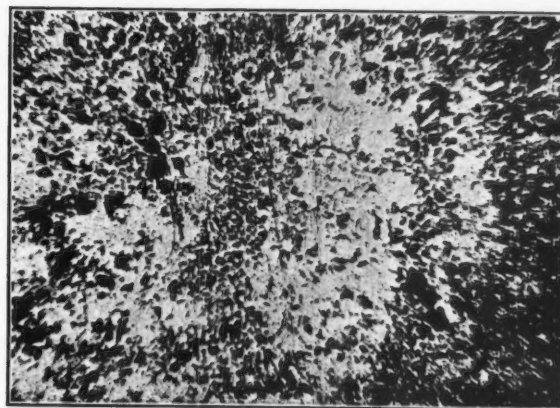


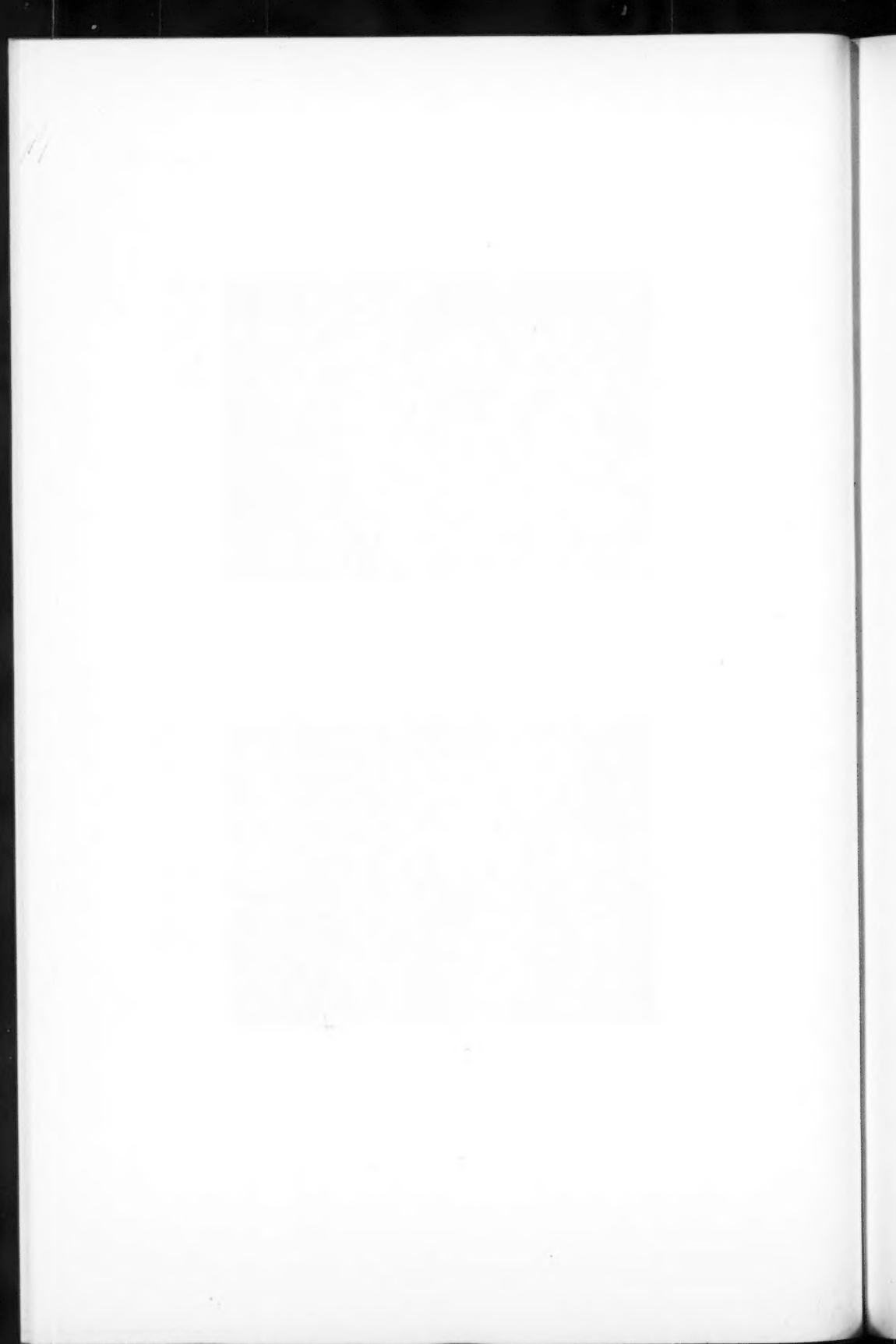
PLATE VII



No. 18. Vanadium steel casting.  $\times 100$ .  
Heated to  $1750^{\circ}\text{F}$ . and cooled in air,  
reheated to  $1450^{\circ}\text{F}$ ., cooled in air from  
 $1450^{\circ}\text{F}$ .



No. 19. Nickel-vanadium steel casting.  $\times 100$ .  
Heated to  $1750^{\circ}\text{F}$ . and cooled in air,  
reheated to  $1450^{\circ}\text{F}$ ., cooled in air  
from  $1450^{\circ}\text{F}$ .





The bars, from which the specimens for No. 8, 10, 12, 13 and 14 were made, were heated to 1660° F. for 3 hr., then cooled, in the furnace to 1100° F. and from 1100° F. in air. The fractures of the specimens showed a fine-grained structure, and all of the specimens were tough and ductile. The decrease in impact resistance, between room temperatures and the lowest temperatures at which the specimens were tested, varied from 54% to 36%.

The bars from which the specimens of No. 11 were made, were duplicates of No. 10, but did not receive any heat treatment. The marked effect of heat treatment is quite noticeable. A large decrease in impact resistance is shown at the various temperatures. The fractures showed a very coarse grain. The specimens were not nearly so tough and ductile as those of No. 10.

The bars for No. 12, 13 and 14 were of slightly different chemical composition. They were given the same heat treatment, and were tested at the two temperatures indicated in Table VI. While there is a considerable variation in impact resistance, the strength at the low temperature -70° F. is quite high. The microphotographs of these specimens are shown on Plates IV and V, and the variation with temperature of the impact resistance of No. 10 and No. 11 in Fig. 2.

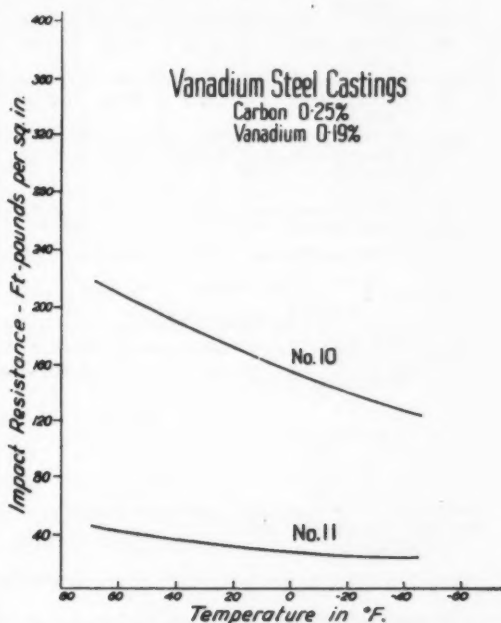


FIG. 2. Effect of low temperatures and heat treatment. No. 10 heated to 1660° F., cooled in the furnace to 1100° F., in air from 1100° F.; No. 11, as cast.

#### (D) Alloys of Steel Castings

Specimens No. 15, 16, 18, 19 and 20 were all alloys of steel. No. 15, 16 and 20 were nickel steel castings; No. 18 vanadium steel castings; and No. 19 nickel-vanadium steel casting.

All specimens for this series were heated to 1750° F., then cooled in air, reheated to 1450° F., and cooled in air from that temperature. Only sufficient material was available to make specimens to test at the two temperatures indicated, 68° and -36° F. All of these specimens were tough and ductile, the fractures were incomplete, and showed a fine grain structure. Plates VI and VII show microphotographs of these specimens. The chemical compositions of these alloys are given in Table VII, the results of the impact tests, in Table VIII.

TABLE VII  
ALLOY STEEL CASTINGS

Specimen No.	Classification of material	Comb. carbon per cent	Silicon per cent	Man-ganese per cent	Sulphur per cent	Phos-phorus per cent	Nickel per cent	Vana-dium per cent
15	Nickel steel casting	0.16	0.35	0.78	0.032	0.015	2.36	—
16	Nickel steel casting	0.24	0.46	0.91	0.026	0.015	2.21	—
20	Nickel steel casting	0.16	0.40	0.88	0.031	0.015	2.69	—
18	Vanadium steel casting	0.34	0.42	0.90	0.026	0.014	—	0.18
19	Nickel-vanadium steel casting	0.18	0.41	0.97	0.031	0.018	1.56	0.10

TABLE VIII  
RESULTS OF TESTS OF THE ALLOY STEEL CASTINGS

Temperature of test, in ° F.	Impact resistance in ft-pounds per sq. in.				
	No. 15	No. 16	No. 18	No. 19	No. 20
68	702	764	530	848	683
-36	473	543	372	758	603
Per cent decrease in impact resistance	32	29	30	10.6	11.7

It was found that resistance to impact of the alloy steel castings was much higher than for the plain carbon steel castings. At room temperature 65° F., the resistance to impact was fairly uniform, 702, 764, 530, 848 and 683 ft-pounds per square inch. Between the temperatures 68° F. and -36° F., the reduction in strength in specimens No. 15, 16 and 18 varied from 29% to 32%. In specimens No. 19 and 20, the decrease in strength was only about 11%. It will be noted that No. 19 contained 1.56% nickel and 0.10% vanadium, while No. 20 contained 2.69% nickel.

(E) *Vanadium Steel Forgings*

The specimens were cut to convenient lengths from bars 1 in. square, before being given the heat treatment.

Heat treatment:

- No. 9      The bars were heated to 1600° F., then cooled in air, reheated to 1500° F., and then cooled in air.
- No. 21-A   Heated to 1650° F., removed from the furnace and cooled in still air, reheated to 1500° F., and cooled in air.

- No. 21-B Heated to 1650° F., cooled in air, reheated to 1250° F., and cooled in air.
- No. 21-C Heated to 1650° F., cooled in air, reheated to 1100° F., and cooled in air.
- No. 21-D As forged.
- No. 21-E Heated to 1650° F., cooled in air, reheated to 1175° F., and cooled in air.
- No. 21-F Heated to 1650° F., cooled in air, reheated to 1300° F., and cooled in air.
- No. 21-G Heated to 1650° F., cooled in air, reheated to 1400° F., and quenched in water at 70° F., reheated to 1250° F., and cooled in air.
- No. 21-H Heated to 1650° F., cooled in air, reheated to 1350° F., then cooled in furnace to 1150° F., and cooled in air from 1150° F.
- No. 21-I Heated to 1650° F., cooled in air, reheated to 1525° F., cooled in furnace to 1250° F., then cooled in air from 1250° F.
- No. 21-J Heated to 1650° F., cooled in air, reheated to 1500° F., and cooled in furnace to 1150° F., then cooled in air from 1150° F.

## Series:

- No. 22-A As forged.
- No. 22-B As forged.
- No. 22-C Heated to 1650° F., cooled in still air, reheated to 1500° F., cooled in furnace to 1100° F., and then cooled in air from 1100° F.
- No. 22-D Heated to 1650° F., cooled in still air, reheated to 1400° F., and then cooled in air.
- No. 22-E Heated to 1650° F., cooled in still air, reheated to 1500° F., and then cooled in air from 1500° F.
- No. 22-F Heated to 1650° F., cooled in still air, reheated to 1400° F., cooled in furnace to 1100° F., cooled in air from 1100° F.

Table IX gives the chemical composition of the bars, and Tables X and XI give the results of tests. The tensile properties of 21-A, B and C are given in Table X.

From an examination of the results of tests on 21-A, B and C, it will be seen that by heat treatment the yield point may be raised, and the ultimate tensile strength increased; by so doing, however, the elongation and reduction in area are decreased, in other words ductility is sacrificed. The impact resistance of 21-A is much higher than that of 21-B and C, but B and C have a higher yield point and higher ultimate tensile strength.

Probably the most remarkable beneficial effect of heat treatment is found in 21-G. Comparing the impact resistance of 21-G with 21-D, where the specimens were tested as forged, it is found that the impact resistance is nearly

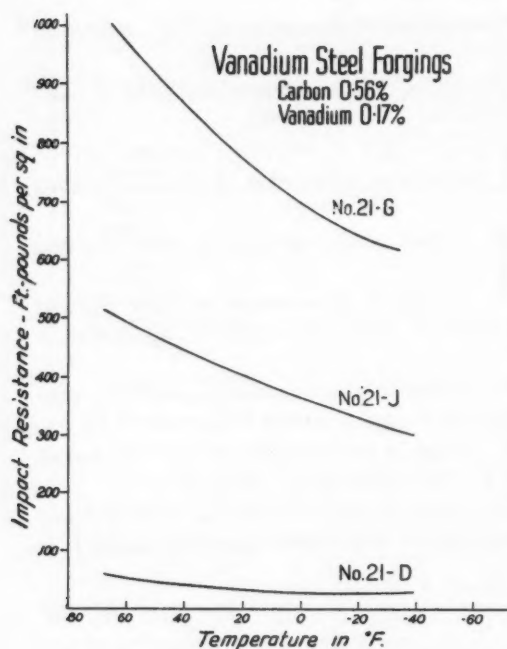


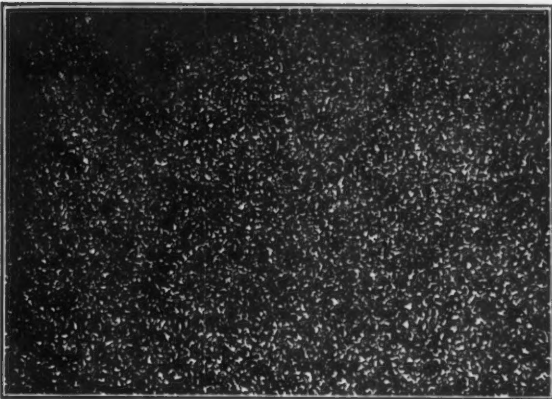
FIG. 3. Effect of low temperatures and heat treatment. No. 21-G, normalized at 1650° F., reheated to 1400° F., quenched in water at 70° F., reheated to 1250° F., cooled in air from 1250° F.; No. 21-J, normalized at 1650° F., reheated to 1500° F., cooled in the furnace to 1150° F., in air from 1150° F.; No. 21-D, as forged.

20 times greater at 68° F. and 34 times greater at -40° F. All fractures of 21-G were incomplete, and showed great toughness and ductility. The fractures of 21-D showed a very coarse crystalline structure. The heat treatment given to 21-G, namely, heating to 1650° F., cooling in air, reheating to 1400° F., quenching in water at 70° F., followed by reheating to 1250° and cooling in still air, gave very high resistance to impact (Fig. 3). This heat treatment for steel castings is not recommended unless care is taken to relieve all internal stresses after quenching. The microphotographs on Plates VIII and IX show the degrees of refinement of the structure of the specimens.

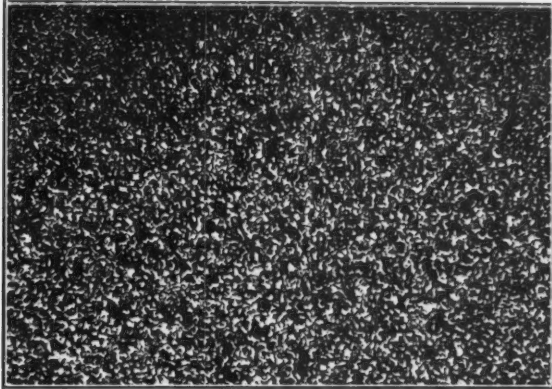
TABLE IX  
VANADIUM STEEL FORGINGS

Specimen No.	Classification of material	Combined carbon per cent	Silicon per cent	Manganese per cent	Sulphur per cent	Phosphorus per cent	Vanadium per cent
9	Vanadium steel forging	0.46	0.29	0.86	0.02	0.03	0.19
21	Vanadium steel forging	0.56	0.26	1.07	0.05	0.05	0.17
22	Same stock bars as No. 21						

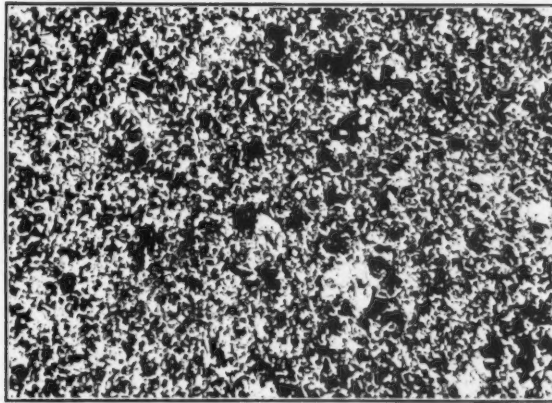
PLATE VIII



No. 21-A. Vanadium steel forging.  $\times 100$ .  
Heated to  $1650^{\circ}\text{F}$ ., removed from  
furnace and cooled in still air;  
reheated to  $1500^{\circ}\text{F}$ ., and cooled in  
air.



No. 21-B. Vanadium steel forging.  $\times 100$ .  
Heated to  $1650^{\circ}\text{F}$ ., cooled in air;  
reheated to  $1250^{\circ}\text{F}$ ., and cooled in  
air.

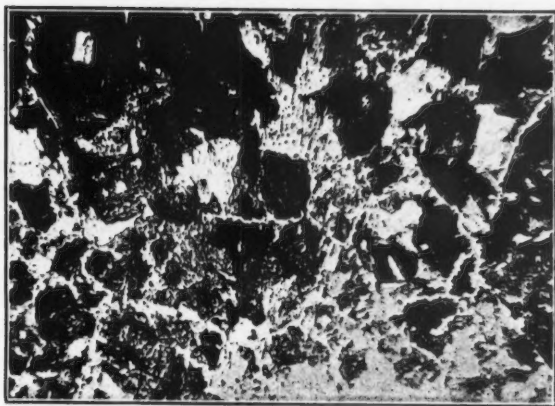


No. 21-C. Vanadium steel forging.  $\times 100$ .  
Heated to  $1650^{\circ}\text{F}$ ., cooled in air;  
reheated to  $1100^{\circ}\text{F}$ ., and cooled in  
air.

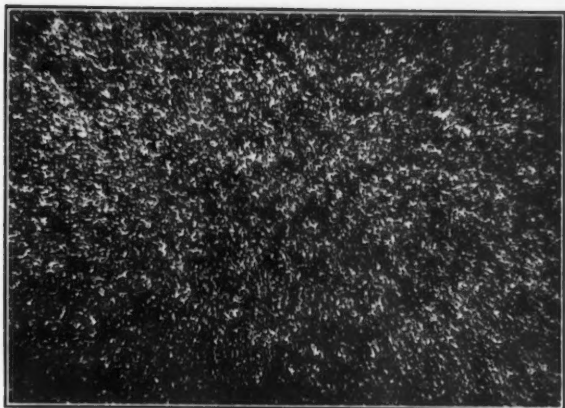




PLATE IX



No. 21-D. Vanadium steel forging.  $\times 100$ .  
As forged.



No. 21-G. Vanadium steel forging.  $\times 100$ .  
Heated to 1650° F., cooled in air;  
reheated to 1400° F., and quenched  
in water at 70° F., reheated to 1250°  
F., and cooled in air.



TABLE X  
RESULTS OF TENSILE TESTS ON ALLOY STEEL FORGINGS

Specimen No.	Vanadium steel forgings	Yield point, in pounds per sq. in.	Ultimate tensile strength, pounds per sq. in.	Elongation (over 2 in.) in per cent	Reduction in area, per cent
21-A	0.56C - 0.17V	77,000	107,000	26	51
21-B	0.56C - 0.17V	78,375	112,500	24	50
21-C	0.56C - 0.17V	80,750	118,500	19.5	49.5

### Discussion of Results

#### 1. Grey Iron Castings

Grey cast irons show a very low resistance to impact at room temperatures. The impact resistance decreases at temperatures below freezing, but, owing to the low impact value, the results are not very reliable. The material is very brittle when subjected to impact. The fractures have a blackish coarsely crystalline appearance. The higher combined carbon specimens have the higher impact resistance. Light castings of grey iron are unsuitable for articles subjected to shock.

#### 2. Plain Carbon Steel Castings

Plain carbon steel castings show a much higher resistance to impact than the grey cast irons. The low carbon steel castings have a higher resistance to impact than the high carbon castings. Heat treatment has a very beneficial effect, especially when tested at the low temperatures. The impact resistance of the heat-treated specimens tested at low temperatures, is nearly three times that of the untreated specimens, as shown by the results of No. 6 and 7. The impact resistance of the heat treated specimens at  $-4^{\circ}$  F. compares favorably with the impact resistance of the untreated specimens tested at room temperatures. The increase in impact resistance at low temperatures due to heat treatment is nearly 300%. The fractures, and the photomicrographs of No. 6 and No. 7, show clearly the marked effect of heat treatment on the crystalline structure.

#### 3. Vanadium Steel Castings

Vanadium steel castings, heat treated, have a very much higher impact resistance at room temperatures than the plain carbon steel castings. When tested at low temperatures the impact resistance compares favorably with the plain carbon castings heat treated and tested at ordinary room temperatures. Vanadium steel castings, heat-treated, are tough and ductile, the fractures show fine-grained structures.

Vanadium steel forgings give more uniform values at the low temperatures. The mechanical working has a tendency to produce a finer grain. The results of tests show the effect of heat treatment, and indicate a beneficial, although

TABLE XI  
RESULTS OF TESTS OF VANADIUM STEEL FORGINGS

Specimen No.	Brinell No.	Temp. of test in ° F.	Impact resistance ft-pounds per sq. in.	Heat treatment
21-A	187	68	252	Heated to 1650° F., cooled in still air, reheated to 1500° F., cooled in air.
21-B	196	68	125	Heated to 1650° F., cooled in air, reheated to 1250° F., cooled in air.
21-C	228	68	64	Heated to 1650° F., cooled in air, reheated to 1100° F., cooled in air.
21-D	286	68 23 -15 -40	55 35 23 18	As forged
21-E	228	68 23 -13 -58	219 193 163 61	Heated to 1650° F., cooled in air, reheated to 1175° F., cooled in air.
21-F	196	68 23 -15 -58	310 264 234 213	Heated to 1650° F., cooled in air, reheated to 1300° F., cooled in air.
21-G	162	68 23 -13 -35	1018 780 660 616	Heated to 1650° F., cooled in air, reheated to 1400° F., quenched in water at 70° F., reheated to 1250° F., cooled in air.
21-H	164	68 23 - 4 -40	509 448 337 260	Heated to 1650° F., cooled in air, reheated to 1350° F., cooled in furnace to 1150° F., cooled in air from 1150° F.
21-I	170	68 23 - 4 -40	448 341 320 305	Heated to 1650° F., cooled in air, reheated to 1525° F., cooled in furnace to 1250° F., cooled in air from 1250° F.
21-J	170	68 23 - 4 -40	510 428 355 300	Heated to 1650° F., cooled in air, reheated to 1500° F., cooled in furnace to 1150° F., cooled in air from 1150° F.
22-A	286	63 -40	84 26	As forged.
22-B	286	63 -40	84 26	As forged.
22-C	168	63 -40	473 353	Heated to 1650° F., cooled in air, reheated to 1500° F., cooled in furnace to 1100° F., cooled in air from 1100° F.
22-D	168	63 -40	453 372	Heated to 1650° F., cooled in air, reheated to 1400° F., cooled in air.
22-E	170	63 -40	494 377	Heated to 1650° F., cooled in air, reheated to 1500° F., cooled in air.
22-F	172	63 -40	397 265	Heated to 1650° F., cooled in air, reheated to 1400° F., cooled in furnace to 1100° F., cooled in air from 1100° F.

probably not the best, heat treatment for material of similar composition. Normalizing at 1600 to 1650° F., followed by reheating to 1150 to 1300° F., and cooling in still air is recommended. The quenched specimens, 21-G gave the highest resistance to impact, also the greatest refinement in the grain structure. This treatment would probably not be practicable with castings having sudden changes in cross section. After quenching, care should be taken to relieve the internal stresses in the metal.

By proper heat treatment it is possible to get a higher yield point, and also higher ultimate strength, but by so doing the elongation and reduction in area are decreased. Greater ductility and higher impact resistance may be obtained, with a slightly lower yield point and tensile strength.

#### 4. Nickel Steel Castings

Nickel steel castings having from 2 to 3% nickel have about the same impact resistance as vanadium steel castings containing from 0.18 to 0.22%. The material when heat-treated is tough and ductile, and has a fine grain structure. It will be noticed also that the nickel steel castings were heated and drawn at higher temperatures than the straight carbon and vanadium steel castings.

The nickel-vanadium steel castings gave the highest impact resistance. Only one nickel-vanadium steel casting was tested containing 1.56% nickel and 0.10% vanadium. The decrease in impact resistance at the low temperature was very small; this shows a great possibility for this material, when subjected to shock at low temperatures.

### Conclusions

From the results of the investigation the following conclusions have been drawn:

Grey iron castings have low impact resistance at room temperatures. The impact resistance decreases for temperatures below freezing.

The impact resistance of straight carbon steel castings, not heat treated, decreases for temperatures below freezing. The impact resistance at temperature below -25° F. may be only one-quarter to one-half the impact resistance at room temperatures.

Heat treatment of straight carbon steel castings increases the impact resistance at room temperatures and temperatures below freezing. The impact resistance of heat-treated specimens at -40° F., compares favorably with the impact resistance of untreated specimens at room temperatures. The low carbon castings have a higher impact resistance than the high carbon castings.

Vanadium steel castings give higher and more uniform values for impact resistance at all temperatures, also greater toughness and ductility, and are to be preferred to the straight carbon castings.

Greater ductility and higher impact resistance may be obtained by proper heat treatment. A slightly lower yield point and tensile strength may be necessary to obtain the desired results.

Normalizing and reheating are recommended as a satisfactory heat treatment to increase the impact resistance at low temperatures.

Nickel and nickel-vanadium steel castings, normalized and reheated, give high impact resistance at low temperatures.

### Acknowledgment

The author wishes to express grateful appreciation to those commercial organizations who have offered suggestions and donated material, particularly Manitoba Steel Foundries, Limited, Selkirk, Manitoba; Vulcan Iron Works, Winnipeg; Canadian National Railways, Transcona Shops; and Canadian Steel Foundries, Montreal. His thanks are also due to Professor Frank Ailen, Department of Physics, University of Manitoba, and many others for their valuable advice and suggestions.

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# THE MECHANISM OF THE FORMATION OF THIURAM AND XANTHOGEN MONOSULPHIDES, AND OBSERVATIONS ON THIOCARBAMYL THIOCYANATES<sup>1</sup>

BY ADRIEN CAMBRON<sup>2</sup>

## Abstract

The mechanism of the desulphurizing action of alkali cyanides on thiuram and xanthogen disulphides has been determined. The reaction is shown to take place in two steps, the intermediate products formed in the first step have been identified as disubstituted thiocarbamyl thiocyanates. These thiocyanates belong to a hitherto unknown series of organic sulphur compounds.

Two methods for the preparation of the new thiocarbamyl thiocyanates are described.

The mechanism of the formation of monoxanthogens by the action of acid chlorides on xanthates is shown to be similar to the formation of monosulphides by the action of cyanides on disulphides.

The following new compounds are described: mixed thioanhydride of ethyl carbonic and isopropyl xanthic acids,  $C_2H_5OC(O)S.CS.OC_3H_7$ , liquid; methyl phenyl thiocarbamyl isopropylxanthyl sulphide,  $C_6H_5(CH_2)N.CS.S.CS.OC_3H_7$ , m.p.  $42^\circ C.$ ; ethylphenyl thiocarbamyl isopropylxanthyl sulphide,  $C_6H_5(C_2H_5)N.CS.S.CS.OC_3H_7$ , m.p.  $41^\circ C.$ ; methylphenyl thiocarbamyl thiocyanate  $C_6H_5(CH_2)N.CS.SCN$ , m.p.  $113.5-114^\circ C.$ ; ethylphenyl thiocarbamyl thiocyanate,  $C_6H_5(C_2H_5)N.CS.SCN$ , m.p.  $75.5^\circ C.$ ; methyl *p*-tolyl thiocarbamyl thiocyanate *p*- $CH_3C_6H_4(CH_2)N.CS.SCN$ , m.p.  $116.5^\circ C.$ ; methyl *p*-tolyl thiocarbamyl chloride, *p*- $CH_3C_6H_4(CH_2)N.CS.Cl$ , m.p.  $53-54^\circ C.$ ; ethyl *o*-tolyl thiocarbamyl chloride, *o*- $CH_3C_6H_4(C_2H_5)N.CS.Cl$ , m.p.  $69^\circ C.$ ;  $\alpha'$  methylphenyl  $\alpha''$  phenyl dithiobiuret,  $C_6H_5(CH_2).N.C.S.NH.CS.NHC_6H_5$ , m.p.  $123^\circ C.$

In previous communications by Whitby and Greenberg (15) and by Cambron and Whitby (3) it was shown that disulphides of the type  $(RO.CS)_2S_2$  (xanthogen disulphides) can be converted into the corresponding monosulphides,  $(RO.CS)_2S$ , by treatment with alkali cyanides. It had earlier been shown by von Braun and Stechele (12) that disulphides of the type  $(R_2N.CS)_2S_2$  (thiuram disulphides) can be similarly converted into the corresponding monosulphides. These reactions can be represented simply as follows:



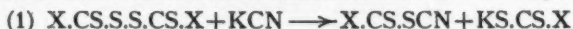
but the mechanism of the reactions remained obscure. Von Braun and Stechele concluded that the thione sulphur was not involved in the conversion of thiuram di- to mono-sulphides, since a similar removal of one atom of sulphur occurred, they found, when isothiuram disulphides,  $(RN:C(SR')S)_2$ , were treated with potassium cyanide. These authors remarked that the absence of any analogous reaction made it extremely difficult to form a plausible idea of the mechanism of the desulphurization, but offered as a speculation the idea that reduction of the disulphide to the free acid was the first step and that the acid was then converted into the monosulphide or thioanhydride by loss of hydrogen sulphide.

<sup>1</sup> Manuscript received May 5, 1930.

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The present research indicates with considerable conclusiveness that the reaction takes place in two stages, as follows: (1) formation of a molecule of a thiocyanate and of a molecule of the alkali salt of the xanthic or dithiocarbamic acid, (2) interaction of these with the elimination of alkali thiocyanate, thus:



A study of the literature concerning the action of alkali cyanides on organic sulphur compounds showed that treatment of benzyl thiosulphate with sodium cyanide brings about scission of a -S-S- linkage, in accord with the following equation (2):



In the benzyl thiocyanate thus formed the SCN radical is attached to an electro-positive radical,  $\text{C}_6\text{H}_5\text{CH}_2\cdot$ , and the compound is relatively stable. A similar reaction on the part of xanthogen and thiuram disulphides would lead to the formation of a thiocyanate in which the SCN radical would be attached to an electro-negative radical,  $\text{RO.CS.}$  or  $\text{R}_2\text{N.CS.}$ , and it would be expected that the halogen-like SCN radical in such a combination would, like Cl in acid chlorides, be very reactive. And, since a molecule of alkali xanthate or dithiocarbamate would be formed simultaneously with the thiocyanate, interaction of the initial products of the reaction would occur. The experimental work confirmed this reasoning, and showed that the two reactions, (1) and (2), mentioned above, follow each other, with the result that the monosulphide and potassium thiocyanate are the ultimate products.

In order to find out whether the above scheme was correct, attempts were made to isolate the thiocyanogen derivative of ethyl and of isopropyl xanthic acids. Two methods were tried: (a) By acting on the ethyl or isopropylchlorthione carbonates of Klason (7) with sodium thiocyanate in absolute alcohol, the expected reaction being:



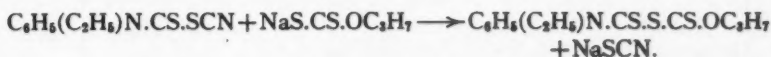
(b) By acting on ethyl and isopropyl xanthates with cyanogen bromide in benzene:



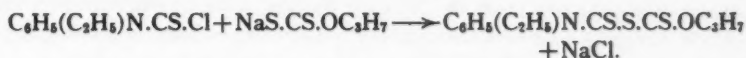
Neither of these two reactions gave definite results, although positive indications were obtained that a benzene soluble thiocyanogen derivative was formed. Since, however, the thiocarbamyl chlorides of Billeter (1),  $\text{R}_2\text{N.CS.Cl}$ , are considerably more stable than the corresponding xanthogen derivatives, i.e., the chlorthione carbonates, (7),  $\text{RO.CS.Cl}$ , it was expected the thiocarbamyl thiocyanates,  $\text{R}_2\text{N.CS.SCN}$ , if such compounds are capable of existence, would be more stable than the thiocyanogen thione carbonates,  $\text{RO.CS.SCN}$ . This view proved to be correct, and the first member of this hitherto unknown series of organic sulphur compounds, the thiocarbamyl thiocyanates,  $\text{RR}'\text{N.CS.SCN}$ , was isolated as a well defined crystalline solid by the action of KSCN on ethyl-phenyl thiocarbamyl chloride in absolute alcohol.



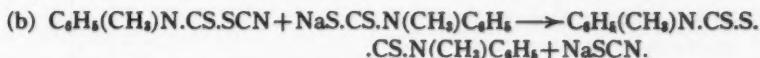
Such thiocarbamyl thiocyanates were found to react with alkali xanthates and dithiocarbamates with the elimination of alkali thiocyanate and the formation of a monosulphide. On treating ethylphenyl thiocarbamyl thiocyanate with sodium isopropyl xanthate in alcohol, an intense yellow color was immediately produced, and on standing there crystallized out a yellow solid consisting of the mixed thioanhydride of ethylphenyl dithiocarbamic and isopropyl xanthic acids. The mother liquor contained sodium thiocyanate. The reaction is as follows:



The identity of the monosulphide thus obtained was established by preparing the same product by the action of ethylphenyl thiocarbamyl chloride on sodium isopropyl xanthate, the reaction being,

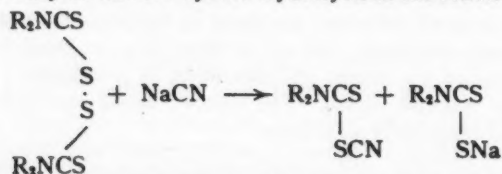


As such mixed anhydrides are new compounds, not described in the literature, it was decided to prepare a known, symmetrical thioanhydride by a similar procedure. This had not been done before because there is no satisfactory procedure described in the literature for the preparation of pure sodium arylalkyl dithiocarbamates. This difficulty was overcome when it was found that sodium arylalkyl dithiocarbamates could be conveniently prepared in a pure state by the action of sodium sulphide on the new arylalkyl thiocarbamyl thiocyanates. Consequently the following experiment was carried out: a solution of sodium methylphenyl dithiocarbamate was prepared by the action of sodium sulphide (1 mol) on the corresponding thiocarbamyl thiocyanate in alcohol. To a measured fraction of the sodium dithiocarbamate solution thus obtained was added an equivalent amount of methylphenyl thiocarbamyl thiocyanate. The product from this reaction was identified as methylphenyl thiuram monosulphide, melting at  $149^\circ\text{C}$ ., the monosulphide being obtained in a yield of 90.5%, as calculated from the following equations:



That the solution obtained by the action of sodium sulphide on the thiocyanate actually contained sodium methylphenyl dithiocarbamate was proved by diluting the remaining fraction with water, and then treating the clear solution with an aqueous solution of cyanogen bromide, in order to oxidize any dithiocarbamate present to the insoluble disulphide (3). The addition of the bromide caused the precipitation of a colorless crystalline solid which was identified as methylphenyl thiuram disulphide, the latter being obtained in a yield of 89%, based on the amount of this carbamyl thiocyanate originally used.

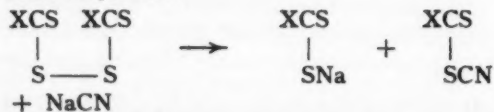
The above experiments show that xanthogen and thiuram disulphides can undergo what may be termed 'cyanic' hydrolysis in the following manner:



The products formed would immediately interact to form the corresponding monosulphide by the elimination of sodium thiocyanate and hence experimental evidence of the formation of the thioacyl thiocyanate in the first stage of the reaction would be very difficult to secure. The following analogies will show, however, that the addition of NaCN to the disulphide bond in xanthogen and thiuram disulphides must be expected to take place in the manner indicated. When bromine and sodium cyanide are allowed to react in molecular proportion, cyanogen bromide is formed:



The displacement of the CN group from its salt by bromine is obviously due to the fact that the latter has a greater electron affinity than the former, or in other words, Br is negative to CN. But it can also be shown that, with respect to electron affinity or electro-negative character, the X.CS.S- group is in the same position relatively to the CN group, as Br is to the latter, for CN will not displace the X.CS.S- radical from its salts, at least in the case of dithiocarbamates and xanthates. (Cyanogen gas was found to be without action on sodium isopropyl xanthate and on sodium methylphenyl dithiocarbamate.) Consequently it would be expected that the same reaction would take place between a xanthogen or thiuram disulphide and sodium cyanide as between bromine and sodium cyanide:

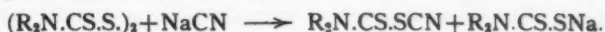


It will be noted that the disulphide molecule behaves very much like a halogen molecule in the above reaction, this being apparently due to a similarity between the disulphide bond in compounds of this type and the interatomic bond in the free halogens. That sulphur can assume a halogen-like valence has been well brought out by the work of Soderback (10) on free thiocyanogen, also the more recent work of Lecher and Simon (8). The latter showed that free thiocyanogen contained a disulphide bond, (its structure corresponding to the formula:  $\text{NCS}-\text{SCN}$ ), and concluded that the energy value of this disulphide bond was of the same order as that of the interatomic bond in elementary halogens. Soderback, basing his conclusions on the stability of some thiocyanates (10), placed free thiocyanogen between Br and I in the electrochemical table, and it is interesting to note that this position corresponds to

that given to the same radical by Bjerrum and Kirschner (2) on electrochemical grounds. Since the  $X.CS.S-$  radical is displaced from its salts by I, this radical would be assigned a position below I in the table. In order to explain the reaction between alkali cyanides and xanthogen or thiuram disulphides, which has been shown to be the first step in the desulphurization process, one must assume that the disulphide molecule first splits into free radicals, which must be capable of at least momentary existence. It may be interesting to note at this point that Gomberg (5) recently stated that it is becoming more and more customary to interpret the mechanism of many reactions by assuming that the reacting molecules first split up into free radicals, the latter then uniting to form new molecules, the nature of the products being governed by the relative electron-affinities of the radicals initially formed.

#### Action of Alkali Cyanides on Organic Disulphides of the Type RSSR.

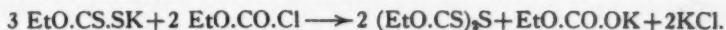
Organic disulphides of the type RSSR, where R is an alkyl or an aryl radical, are not desulphurized by alkali cyanides in alcoholic solution, and this would appear to be somewhat abnormal, in view of the readiness with which thiuram and xanthogen disulphides are converted to the monosulphides by the same reagent. The following considerations will show, however, why desulphurization in this case cannot take place. The first step in the desulphurization of thiuram and xanthogen disulphides by alkali cyanides can be considered as the displacement of the cyanogen radical from its salt by the stronger electro-negative radical  $X.CS.S-$ ,



If we now consider the case of aryl or alkyl disulphides, it becomes at once obvious that a similar reaction cannot take place, because the  $RS-$  radical is positive with respect to  $CN-$ , and consequently cannot displace the latter from its salts. If this is true, one would expect the reverse reaction to be possible, that is, it should be possible to displace the  $RS-$  radical from its salts by  $CN-$ . This actually was found to be the case, phenyl disulphide was obtained in nearly theoretical yield by the action of cyanogen gas on an aqueous solution of sodium phenyl mercaptide.

#### Mechanism of the Formation of Xanthogen Monosulphides by Other Reactions

Ethyl xanthogen monosulphide was prepared by Welde (13) by the action of ethyl chlorocarbonate on potassium ethyl xanthate. This author represented the reaction by the following equation:



This equation involves the replacement of a carbonyl oxygen by an atom of sulphur. Yet the reaction takes place readily at room temperature. The equation must be considered as lacking in a priori probability. Willcox (14)



suggested that the reaction involved (a) the formation of an unsymmetrical anhydride and subsequently (b) the spontaneous breakdown of the latter into a mixture of two symmetrical anhydrides, thus:



Holmberg (6, p. 278) has however shown that the mixed anhydride in question is a relatively stable compound which can be distilled at 149°/50 mm. without decomposition.

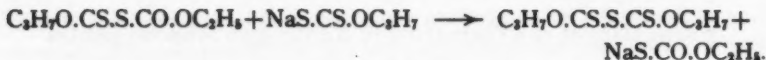
Now it has been shown (*supra*) that the thiocyanates,  $\text{RO.CS.SCN}$  and  $\text{R}_3\text{N.CS.SCN}$ , which may be regarded as mixed anhydrides of xanthic and dithiocarbamic acids on the one hand and thiocyanic acid on the other hand, react with alkali xanthates and dithiocarbamates to form the monosulphides or symmetrical anhydrides. By analogy, it was thought possible that mixed anhydrides formed by the action of chlorocarbonates on xanthates might react with xanthates to form xanthogen monosulphides. This has been proved experimentally, and hence the mechanism followed in Welde's reaction for the preparation of xanthogen monosulphides may be written as follows:



The action of ethyl chlorocarbonate on sodium isopropyl xanthate in dry acetone at -5° C. yielded the mixed thioanhydride as a pale yellow oil in 98.5% yield,

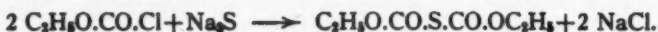


On adding one mol of this anhydride to an alcoholic solution of one mol of sodium isopropyl xanthate, an intense yellow color was immediately produced, and, after the solution had stood for some time at room temperature, isopropyl xanthogen monosulphide crystallized out as a clear yellow solid. The yield of isopropyl monoxanthogen was 69.1%, as calculated from the following equation:



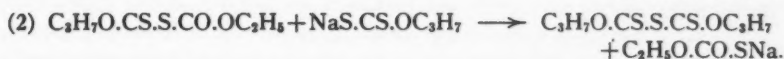
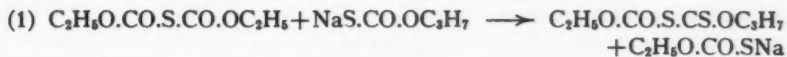
The magnitude of the yield of xanthogen monosulphide clearly indicates that the product cannot have arisen, as Willcox believed, by decomposition of the mixed anhydride alone.

Further evidence that the reaction follows the course stated was obtained in the following experiment. The thioanhydride of ethyl thiolcarbonic acid was prepared, according to Holmberg's method (6), by the action of sodium sulphide on ethyl chlorocarbonate:



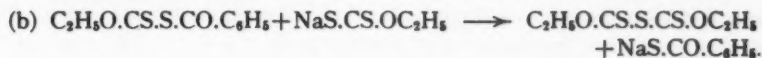


On treating the product with sodium isopropyl xanthate in alcohol, isopropyl xanthogen monosulphide was obtained in 34.5% yield. The reaction in this case may be considered as taking place in the following two steps:

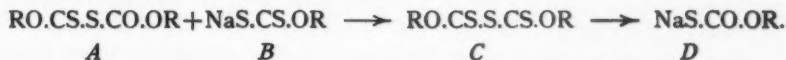


It is clear that the xanthogen monosulphide obtained in this experiment must have come from the sodium salt, since the anhydride used did not contain the isopropyl group. The mother liquor from the reaction was examined for the presence of sodium ethyl thiocarbonate by the addition of an oxidizing agent (sodium tetrathionate), but, although the formation of a water insoluble oil indicated the result expected, the product was contaminated with some isopropyl xanthogen disulphide, formed by oxidation of unchanged xanthate, which could not be removed completely.

By using benzoyl chloride instead of a chlorocarbonate, however, for the preparation of a xanthogen monosulphide from a xanthate, more conclusive results were obtained in regard to the identification of the water soluble reaction product. Tschugaeff (11) has shown that benzoyl chloride reacts with xanthates, under the same conditions as chlorocarbonates, to form xanthogen monosulphides. The mechanism of the reaction is undoubtedly similar in both cases. The following experiment was carried out. Two mols of sodium ethyl xanthate was added to an acetone solution of one mol of benzoyl chloride, and after reaction was complete, the xanthogen monosulphide was precipitated by the addition of water, and was filtered off. The mother liquor was then treated with an aqueous solution of sodium tetrathionate, in order to oxidize any sodium thiobenzoate present to the corresponding disulphide\*. The result was the precipitation of a solid product, which, after recrystallization from alcohol, was identified as benzoyl disulphide. Consequently, sodium thiobenzoate is formed as a by-product when ethyl xanthogen monosulphide is prepared by the action of benzoyl chloride on sodium ethyl xanthate, and the following equations represent the course of the reaction:



The reaction between mixed thioanhydrides of the type  $\text{RO.CS.S.CO.OR}$  and alkali xanthates is a reversible one, as a consideration of the compounds involved will show:



\* In a previous communication (3) it was shown that sodium tetrathionate oxidises salts of dithio acids to the corresponding disulphides. It has also been found that the same reagent can be used for the oxidation of salts of thioacids, such as thiobenzoic acid, to the disulphides.

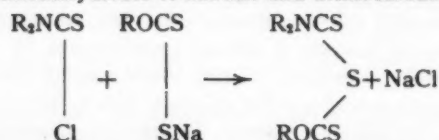
It is clear that the same equilibrium mixture would be obtained if, instead of starting from equimolecular quantities of *A* and *B*, the reactions were started from the same relative amounts of *C* and *D*. The relative amounts of *B* and *D* present at equilibrium would depend, in the above example, on the relative strength of the acids  $\text{RO.CS.SH}$  and  $\text{RO.CO.SH}$ . This may be illustrated by consideration of the case of the reaction between one of the new thiocarbamyl thiocyanates, which is a mixed anhydride derived from dithiocarbamic acid, a relatively weak acid, and thiocyanic acid, a strong acid, and the corresponding sodium dithiocarbamate:



The reaction here goes almost quantitatively from left to right, because the dithiocarbamic acid is a very weak acid compared to thiocyanic. The difference between the strength of the acids  $\text{RO.CS.SNa}$  and  $\text{RO.CO.SNa}$  is probably relatively small, and it is probable that yields of monoxanthogen obtained in the reaction between chlorocarbonates and xanthates would be lower than those actually observed, were it not that the decomposition of one of the products, such as the sodium thiol carbonate which is fairly unstable, appears to favor the reaction from left to right.

#### Mixed Anhydrides of Xanthic and Dithiocarbamic Acids

Having had occasion to prepare a number of disubstituted thiocarbamyl chlorides for the investigation of carbamyl thiocyanates, it was thought of interest to determine whether these chlorides would react with alkali xanthates to form mixed thioanhydrides of xanthic and dithiocarbamic acids, as follows:



and two members of this new series of mixed thioanhydrides were prepared, viz., that derived from isopropyl xanthic and ethylphenyl dithiocarbamic acid:  $\text{C}_6\text{H}_5(\text{C}_2\text{H}_5)\text{N.CS.S.CS.OC}_3\text{H}_7$ , and the corresponding methylphenyl compound:  $\text{C}_6\text{H}_5(\text{CH}_3)\text{N.CS.S.CS.OC}_3\text{H}_7$ . It was found possible to prevent any secondary reaction between the mixed anhydride and the sodium xanthate by carrying out the preparation at low temperature.

It was noted that these asymmetrical thioanhydrides have melting points lower than that of isopropyl monoxanthogen; the ethylphenyl compound melts at  $40.5-41^\circ\text{C}$ ., and the methylphenyl compound at  $42^\circ\text{C}$ ., while isopropyl monoxanthogen melts at  $55^\circ\text{C}$ ., ethylphenyl and methylphenyl thiuram disulphides melting at  $115^\circ$  and  $150^\circ\text{C}$ . respectively. This is not without analogy, for Lecher (9) observed the same effect in the case of mixed organic sulphides of the type  $\text{R'SSR}$ . *o*-Nitrophenylphenyl disulphide, for instance, melts at  $55^\circ$ , while phenyl disulphide melts at  $60-62^\circ$ , and *o*-dinitro phenyl disulphide melts at  $198^\circ\text{C}$ .

### Thiocarbamyl Thiocyanates

#### Preparation

The failure of the first attempts to isolate a thio-acyl thiocyanate by the action of cyanogen bromide on alkali xanthates was later found to be due to the presence of water, which favors the action of cyanogen bromide as an oxidizing agent. Even small amounts of water appear to be sufficient to prevent the formation of a thiocyanate by substitution, but this may be explained by the fact that the oxidation reaction is an ionic one (3), and consequently proceeds at a much faster rate than substitution, which is not ionic.

The action of thiocarbamyl chlorides on potassium thiocyanate was later found to be a very convenient method for the preparation of thiocarbamyl thiocyanates. Absolute alcohol was found to be the best solvent in which to carry out the reaction, the latter taking place smoothly at room temperature. Ethylphenyl, methylphenyl and methyl-*p*-tolyl thiocarbamyl thiocyanates were prepared by the same method. An attempt to prepare methyl-*o*-tolyl thiocarbamyl thiocyanate was unsuccessful. It is interesting to note that derivatives of methyl-*p*- and ethyl-*o*-tolyl dithiocarbamic acids are unknown. After preparing without difficulty methyl-*p*-tolyl thiocarbamyl chloride and thiocyanate,  $p\text{-CH}_3\text{C}_6\text{H}_4\text{.}(\text{CH}_2)\text{N.CS.Cl}$  and  $p\text{-CH}_3\text{C}_6\text{H}_4(\text{CH}_2)\text{N.CS.SCN}$ , an attempt was made to prepare the corresponding ethyl-*o*-tolyl compounds. The action of thiophosgene on ethyl-*o*-toluidine yielded ethyl-*o*-tolyl thiocarbamyl chloride satisfactorily, but, when it was attempted to prepare the thiocarbamyl thiocyanate by the action of potassium thiocyanate on the chloride, the result was not satisfactory. The product was an amorphous solid, which could not be crystallized, and which decomposed on standing, but which gave some of the characteristic reactions of carbamyl thiocyanates such as the production of a yellow color when added to an alcoholic solution of an alkali xanthate, and the formation of a deep red color on warming with a few drops of ferric chloride solution. Ortho or para substitution in the phenylalkyl dithiocarbamic acids does not seem to affect the stability of the corresponding carbamyl chloride, while ortho substitution renders the corresponding carbamyl thiocyanate unstable, the para substituted compound being stable. Similarly with regard to the ammonium dithiocarbamates corresponding to these amines, ammonium methyl-*p*-tolyl dithiocarbamate can be isolated, although very unstable, while the corresponding ethyl-*o*-tolyl compound will not form at all.

A second method for the preparation of disubstituted thiocarbamyl thiocyanates was later found. It consists in treating the lead salt of the dithio carbamic acid with cyanogen bromide in anhydrous benzene. The reaction is:



This method is somewhat more convenient than the first as it does not require the preparation of the thiocarbamyl chloride, and consequently the use of thiophosgene. Methylphenyl thiocarbamyl thiocyanate was prepared by this method in good yield.

It may be of interest to remark at this point that under appropriate conditions three different products can be obtained, each in remarkably good yield, by the reaction between cyanogen bromide and metallic dithiocarbamates viz., (a) thiuram disulphides, by carrying out the reaction in water; (b) thiuram monosulphides, by carrying out the reaction in alcohol; (c) thiocarbamyl thiocyanates, by carrying out the reaction in anhydrous benzene. The first and second of these reactions were first described by von Braun and Stechele (12), and Cambron and Whitby (3) have recently shown that, under similar conditions, cyanogen bromide reacts with xanthates to give xanthogen di- and mono-sulphides respectively. The third reaction is new.

#### Reactions

The following characteristic reactions of thiocarbamyl thiocyanates will serve to show the close similarity between the reactivity of the  $-\text{SCN}$  group in these compounds and that of chlorine in acid chlorides.

Both thiocarbamyl chlorides and thiocarbamyl thiocyanates, as stated earlier, react with alkali dithiocarbamates to yield thiuram monosulphides and with alkali xanthates to yield mixed thioanhydrides. With sodium sulphide, the nature of the product obtained depends on the proportion of sulphide used. With one-half mol of sodium sulphide, the thiuram monosulphide is the only product:



With one mol of sodium sulphide, the thioanhydride first formed is reduced to the sodium salt of the acid:



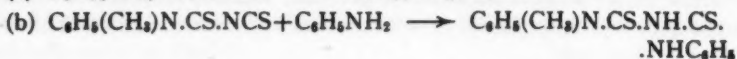
Reactions analogous to these have been observed between acid chlorides and sodium sulphide (6).

#### Conversion of thiocarbamyl thiocyanates to thiocarbimides

A reaction in which, under certain conditions, thiocarbamyl thiocyanates behave differently from the corresponding thiocarbamyl chlorides, is that with aniline. The distinction appears only when the thiocyanates have, by heating, been isomerized to thiocarbimides. At room temperature, both thiocarbamyl thiocyanate and thiocarbamyl chloride react with aniline to form a trisubstituted thio urea as follows:



If, however, the thiocarbamyl thiocyanate is first heated for some time at a temperature close to its melting-point, it no longer reacts in the above manner, but adds on a mol of aniline to form a trisubstituted dithiobiuret. With methylphenyl thiocarbamyl thiocyanate, for instance, the following reaction was obtained after first heating the thiocyanate at  $110^\circ \text{C.}$  for 10 min.,



That an irreversible change in the constitution of thiocarbamyl thiocyanates takes place under the influence of heat is also shown by the fact that on standing for some time at temperatures from 15 to 20° below their melting-points, they are gradually converted into deep red liquids, which show the characteristic reactions of thiocarbimides.

### Experimental

#### PREPARATION OF THIOCARBAMYL THIOCYANATES

##### *Ethylphenyl thiocarbamyl thiocyanate*, $C_6H_5(C_2H_5)N.CS.SCN$ .

Three grams of finely ground potassium thiocyanate were added to a solution of 5 gm. ethylphenyl thiocarbamyl chloride in 25 cc. absolute alcohol, and the mixture allowed to stand for two hours at room temperature with occasional shaking. The solution becomes turbid at first, due to the separation of KCl, then gradually sets to a semi-solid mass of crystals. Water was then added to dissolve the potassium salts and precipitate the thiocyanate, the latter being filtered off. The product is obtained in practically quantitative yield. It crystallizes from warm alcohol in shiny, colorless needles, melting at 75.5-76° C. to a bromine-red oil. It is quite soluble in warm alcohol, more so in ether, and very soluble in chloroform and benzene. The product turns pink after standing for a few days, and is gradually changed over to a clear red oil on standing for some weeks, the change being accelerated by exposure to light. (Indications are that the decomposition of the solid into a red liquid is due to isomerization of the thiocyanate into the thiocarbimide.)

Analysis: .2146 gm. subst. gave .4413 gm.  $BaSO_4$ . Calculated for  $C_{10}H_{10}N_2S_2$ , (M.W. 222.1) 28.80% S; found 28.25%.

Molecular weight determination: .1646 gm. subst. in 17.8767 gm.  $C_6H_6$ , ( $K=51.2$ ), gave  $T_1 - T_0 = 0.208^\circ$ . Calculated for  $C_{10}H_{10}N_2S_2$  M.W. 222.1; found 224.0.

##### *Methylphenyl thiocarbamyl thiocyanate*, $C_6H_5(CH_3)N.CS.SCN$ .

Preparation by the action of KSCN on the carbamyl chloride.

This compound was prepared by acting on methylphenyl thiocarbamyl chloride with KSCN in absolute alcohol, the same procedure as for the preparation of the ethylphenyl compound being followed. This thiocyanate, on recrystallization from warm alcohol, was obtained in the form of lustrous leaflets, melting at 114° C. to a deep red oil. It is less soluble in alcohol than the ethylphenyl compound, but is very soluble in chloroform and benzene. It appears to be much more stable than the ethylphenyl derivative, for a sample which has been standing for two months does not show any signs of discoloration or decomposition.

Analysis: .1223 gm. subst. gave .2696 gm.  $BaSO_4$ . Calculated for  $C_9H_9N_2S_2$  (M.W. 208), 30.83% S; found 30.30%.



#### Preparation by action of CNBr on lead dithiocarbamate.

A solution of 11.5 gm. cyanogen bromide in benzene was dried carefully by allowing it to stand over calcium chloride for two days. To the filtered solution was then added 30 gm. of dry lead methylphenyl dithiocarbamate. After standing for four days the reaction mixture was filtered, and, on evaporation of the solvent, 7.5 gm. of methylphenyl thiocarbamyl thiocyanate was obtained which, after one recrystallization from alcohol, melted correctly at 113.5° C.

#### *Methyl-p-tolyl thiocarbamyl thiocyanate*, $p\text{-CH}_3\text{C}_6\text{H}_4(\text{CH}_3)\text{N.CS.SCN}$ .

2.5 gm. of methyl-*p*-tolyl thiocarbamyl chloride was treated with 2 gm. potassium thiocyanate in absolute alcohol, the reaction product being then precipitated by the addition of water and filtered off. After recrystallization from absolute alcohol, 2.1 gm. of pure thiocyanate was obtained as large shiny plates, melting at 116.5° C. The methyl-*p*-tolyl compound appears to be as stable as the methylphenyl one.

Analysis: .1323 gm. subst. gave .2791 gm.  $\text{BaSO}_4$ . Calculated for  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{S}_2$  (M.W. 222) 29.00% S; found, 28.98.

#### PREPARATION OF SOME NEW THIOCARBAMYL CHLORIDES

##### *Ethyl-o-tolyl thiocarbamyl chloride*, $o\text{-CH}_3\text{C}_6\text{H}_4(\text{C}_2\text{H}_5)\text{N.CS.Cl}$

The above compound, which is not described in the literature, was prepared by von Braun's method (12, p. 2274), by the action of thiophosgene on ethyl-*o*-toluidine in ether. The carbamyl chloride, after recrystallization from low boiling ligroin, was obtained in the form of small plates, melting at 69° C.

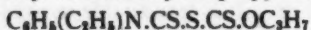
Analysis: .1945 gm. subst. gave .1322 gm.  $\text{AgCl}$ . Calculated for  $\text{C}_{10}\text{H}_{12}\text{NCSCl}$  (M.W. 199.5) 16.61% Cl; found 16.93%.

##### *Methyl-p-tolyl thiocarbamyl chloride*, $\text{CH}_3\text{C}_6\text{H}_4(\text{CH}_3)\text{N.CS.Cl}$ .

This carbamyl chloride is not described in the literature. It was prepared by the same method as the ethyl-*o*-compound, by the action of thiophosgene on methyl-*p*-toluidine in ether, and, on recrystallization from low boiling ligroin, obtained in the form of leaflets melting at 53-54° C.

#### ACTION OF THIOCARBAMYL THIOCYANATES ON ALKALI XANTHATES AND DITHIOCARBAMATES

##### *Phenylethyl thiocarbamyl isopropyl xanthyl sulphide\**,



Two grams phenylethyl thiocarbamyl thiocyanate and 1.75 gm. sodium isopropyl xanthate were dissolved separately in a few cc. absolute alcohol. On mixing the two solutions a yellow color was produced after a few minutes. The reaction mixture was allowed to stand at room temperature for 2 hr.

\* For the purpose of naming this compound the residues  $\text{RO.CS}$ —corresponding to xanthic acids are termed "xanthyl", this designation being analogous to the designation of the  $\text{CH}_3\text{CO}$  residue as "acetyl".

The addition of water to the solution precipitated an oil, which was extracted with ether. On drying the extract and evaporating the ether, the product was again obtained as an oil. It was expected, however, that the product should be a solid, and consequently it was purified by repeatedly dissolving it in alcohol, in which it was very soluble, then precipitating it with water. In this manner about 0.5 gm. of a yellow solid was obtained which, after recrystallization from glacial acetic acid, melted at  $39.5-40^{\circ}\text{C}$ .

Analysis: .1622 gm. subst. gave .3800 gm.  $\text{BaSO}_4$ . Calculated for  $\text{C}_{13}\text{H}_{17}\text{ONS}_3$  (M.W. 299.2) 32.15% S; found 32.18%.

.5268 gm. subst. gave .02552 gm. N. Calculated for  $\text{C}_{13}\text{H}_{17}\text{ONS}_3$ , 4.70; found 4.81% N.

In order to confirm the identity of the above compound, it was prepared by the action of ethylphenyl thiocarbamyl chloride on isopropyl xanthate. Ten grams ethylphenyl thiocarbamyl chloride and 8 gm. sodium isopropyl xanthate were dissolved in 50 cc. absolute alcohol, and the solution allowed to stand for about two hours at room temperature. The addition of water to the alcoholic solution precipitated the product as an oil. The latter was extracted with ether, and, on evaporation of the latter, the mixed anhydride was obtained as a crystalline yellow solid, which after recrystallization from glacial acetic acid, melted sharply at  $41^{\circ}$ . No variation in the melting point was observed after repeated recrystallizations from glacial acetic acid and ligroin. On mixing equal parts of the product obtained in this experiment with that obtained by the action of sodium isopropyl xanthate on ethylphenyl thiocarbamyl thiocyanate the melting point of the latter product was not depressed.

*Phenylmethyl thiocarbamyl isopropyl xanthyl sulphide,*



This sulphide was prepared by the action of phenylmethyl thiocarbamyl chloride on sodium isopropyl xanthate in absolute alcohol, the same procedure as in the preparation of the phenylethyl compound being followed. As in the case of the latter, this compound was first obtained as an oil, but on extraction of the oil with ether, and evaporation of the solvent, it was obtained in the form of a crystalline yellow solid, after recrystallization from glacial acetic, melted at  $42^{\circ}\text{C}$ . In order to show that the product obtained in this reaction was actually the asymmetrical anhydride, and not a mixture of the two symmetrical anhydrides, it was recrystallized several times from glacial acetic acid, but this failed to produce any variation in the melting point.

*Sym. dimethyl diphenyl thiuram monosulphide,  $(\text{C}_6\text{H}_5(\text{CH}_3)\text{NCS})_2\text{S}$ .*

An alcoholic solution of sodium methylphenyl dithiocarbamate was first prepared by the action of sodium sulphide, 1.75 gm., on a solution of 1.50 gm. methylphenyl thiocarbamyl thiocyanate in alcohol. The addition of the sodium sulphide caused the formation of a deep yellow color, which then gradually faded till the solution became almost colorless. The solution was



allowed to stand till a drop of it, added to a few cc. of water gave a clear solution showing that all the thiocyanate had reacted. The solution was then made up to 45 cc. with alcohol. To a measured fraction of this solution, 24 cc., was added 0.8 gm. methylphenyl thiocarbamyl thiocyanate, the solution immediately assuming a deep yellow color. The solution was warmed to about 35° C. to complete the reaction, and on cooling, a yellow crystalline precipitate was formed. An equal volume of water was added to the reaction mixture, the precipitate filtered off and washed free of potassium thiocyanate, (the presence of which in the filtrate could be shown by the addition of a few drops of ferric chloride solution). After recrystallization from alcohol-chloroform, the product melted at 149.5-150° C., which is the correct melting point for sym. dimethyldiphenyl thiuram monosulphide. The identity of the product was confirmed by taking a mixed melting point with a sample of the pure monosulphide, no depression being observed.

In order to prove that the alcoholic solution used in the above experiment actually contained sodium methyl phenyl dithiocarbamate, the remaining fraction, 19 cc., was diluted with 50 cc. water. To the clear solution thus obtained was added one gram of cyanogen bromide in water. A white precipitate was obtained directly which, after two recrystallizations from alcohol-chloroform, melted at 196-197° C., which is the correct melting point for sym. dimethyldiphenyl thiuram disulphide. The yield of thiuram monosulphide obtained in the first part of the experiment was 1.16 gm., or 90.5%, as calculated on the 0.8 gm. of thiocarbamyl thiocyanate used. In the second part of the experiment, the yield of thiuram disulphide obtained was 0.49 gm., or 89%, as calculated on the 0.63 gm. of thiocyanate used.

*Sym. dimethyldi-p-tolyl thiuram monosulphide, (p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)NCS)<sub>2</sub>S*

To a solution of 1.6 gm. methyl *p*-tolyl thiocarbamyl thiocyanate in alcohol was added 1.8 gm. of finely ground sodium sulphide. The solution turned yellow on the addition of the sulphide, but gradually became colorless again. When a drop of the solution no longer gave a turbidity on mixing with water, 1.45 gm. methyl-*p*-tolyl thiocarbamyl chloride dissolved in a few cc. of absolute alcohol in the cold, was added. The solution turned deep yellow on the addition of the chloride, and a yellow crystalline precipitate began to form after a few minutes. After standing for a half-hour, an equal volume of water was added, and the solution filtered. After recrystallization from chloroform, the product was identified as dimethyl di-*p*-tolyl thiuram monosulphide, melting point 143.5-144° C.

CONVERSION OF THIOCARBAMYL THIOCYANATES TO THIOCARBIMIDES

*α-methylphenyl α-phenyl dithiobiuret, C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)N.CS.NH.CS.NHC<sub>6</sub>H<sub>5</sub>.*

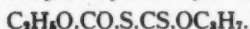
One gram methylphenyl thiocarbamyl thiocyanate was heated in a test tube immersed in an oil bath at 100-110° C. for 10 min. The heating was interrupted when the compound had been completely converted to a dark red oil. The liquid product was dissolved in benzene, and 0.45 gm. aniline added. The

solution was then allowed to evaporate spontaneously and the solid residue recrystallized from alcohol, 0.5 gm. of a light red crystalline product being obtained, melting sharply at 123° C. That the product obtained in this experiment is a dithiobiuret was confirmed by the fact that it is soluble in aqueous alkalis.

Analysis: .0905 gm. subst. gave .1360 gm. BaSO<sub>4</sub>. Calculated for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>S<sub>2</sub> (M.W. 301.1) 21.30% S; found 20.66%.

#### FORMATION OF THIOANHYDRIDES BY METHODS OTHER THAN DESULPHURIZATION

##### *Mixed anhydride from ethyl carbonic and isopropyl xanthic acids,*



A solution of 16 gm. ethyl chlorocarbonate in 40 cc. acetone was added gradually, with mechanical stirring, to a solution of 21 gm. sodium isopropyl xanthate in 50 cc. water, the reaction being carried out at -5° C. There remained only a faint odor of chlorocarbonate after one half-hour stirring. The product was then precipitated by the addition of a large amount of water, separated, and dried under reduced pressure. Yield: 30.4 gm., 98.5% of theory. The product is a pale golden oil.  $n_D$ , 1.5110 at 25.5° C.

##### *Di-isopropyl monoxanthogen, (C<sub>3</sub>H<sub>7</sub>O.CS)<sub>2</sub>S.*

Five grams of the mixed thioanhydride obtained in the above experiment was added to an alcoholic solution of 5 gm. sodium isopropyl xanthate in 20 cc. alcohol. On the addition of the anhydride a deep yellow solution was produced, thus indicating the formation of a xanthogen monosulphide. The solution was allowed to stand overnight, some of the monoxanthogen formed separating out in the form of large crystals. A small amount of water was added to precipitate the monoxanthogen completely, the latter was then filtered off, and recrystallized from alcohol, the yield obtained being 3.9 gm. or 69.1% based on the amount of mixed anhydride used. The recrystallized product showed a melting point of 55-55.5° C., which is the correct melting point for isopropyl monoxanthogen.

Isopropyl monoxanthogen was also obtained in the following manner, by the action of sodium isopropyl xanthate on the thioanhydride of ethyl thiol carbonic acid. A solution of 12.5 gm. sodium isopropyl xanthate in alcohol was added to 14 gm. of the anhydride. As in the preceding experiment, a deep yellow color was immediately produced on mixing the reactants. After standing for some hours the isopropyl monoxanthogen started to crystallize out. The product was completely precipitated by the addition of water, and recrystallized from alcohol. The yield obtained was 3.25 gm., 34.5% of the theory. The purified product showed a melting point of 55° C.

##### *Action of benzoyl chloride on potassium ethyl xanthate.*

This experiment was carried out in order to determine whether sodium thio-benzoate is formed as a by-product in the reaction.

To 14 gm. benzoyl chloride in 75 cc. acetone was added gradually 36 gm. potassium ethyl xanthate. After the xanthate had been all added, the reaction mixture was warmed to 35° C. to complete the reaction. The water insoluble products were precipitated by the addition of water, filtered off, and after recrystallization from alcohol, 11 gm. of pure ethyl xanthogen was obtained. On adding an excess of sodium tetrathionate to the mother liquor, an oil was obtained which, after extraction with ether, washing of the extract, and evaporation of the ether, yielded a crystalline residue which, after two recrystallizations from alcohol, melted at 127° C. On taking a mixed melting point with pure benzoyl disulphide, which melts at 128° C., the melting point of the product was not depressed.

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